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Study of Sulfur Recovery from Coal Refuse

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16. Abstracts A measurement program in San Jose, Calif, during November and December 1970, provided data to evaluate and improve existing receptor-oriented Gaussian diffusion model for calculating urban carbon monoxide (CO) concentrations. Seven stations were operated in a two-block downtown area to measure CO at five heights, winds, and temperature gradients. Co Concentrations and temperatures were also measured by helicopter and two vans. A helical air circulation in the street canyon was observed when roof level winds were within 45° of the cross-street direction. Transport of CO into and out of the downtown area was determined from vertical profiles of wind and horizontal profiles of CO concentrations at various heights up to 300 m along the perimeter of the central area. Evaluation of the revised model has shown that significant improvements have been made. The model reproduces the observed frequency distributions very well for street-canyon sites. At these sites, hourly predictions are well correlated with observations, and about 80 percent of the calculated values are within 3 ppm of the observed, which ranged as high as 16 ppm.

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ABSTRACT

During coal preparation, a coal refuse of no commercial value is produced and discarded in piles. As rainfall percolates through the piles, acid waters are formed.

A feasibility study has been performed on a process producing sulfur from such coal refuse. In this process, limestone and coal refuse are ground, pelletized and preheated before entering a desulfurizing shaft reactor where a hard, fired ash pellet and an H_2S-SO_2 bearing offgas are produced. After sulfur, tar, and other gases are removed, the resulting H_2S-SO_2 gas proceeds to a conventional sulfur recovery plant.

Experimental results and economics of this study indicate that the process is a profitable means of minimizing coal refuse pile water pollution. For a sulfur and ash pellet selling price of $20 and $1.50/ton respectively, it is estimated that a coal producer will have a before tax return on investment up to 53 percent for a one MM ton/year plant utilizing an eight percent sulfur refuse.

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SECTION I

CONCLUSIONS

The experimental results and process economics generated in this feasibility study show that the sulfur recovery process is a profitable means of utilizing coal refuse to recover sulfur. Since the process is economically attractive, it should entice communities and coal producers to utilize rather than stockpile coal refuse; thereby, minimizing water pollution caused by coal refuse. In particular, the following conclusions may be drawn from the results of this study.

1. The experimental laboratory study has shown that commercially feasible operating temperatures (1900-2100°F) and reasonable residence times (30 minutes or less) are required to operate the process. Specifically, the results of experimentation simulating the sulfide formation zone in the shaft reactor show that a residence time of 30 minutes will suffice at 1900°F to yield a maximum conversion of coal refuse sulfur to the sulfide form, and to completely retain the organic sulfur. Experimentation to simulate the desulfurization zone in the shaft reactor has shown that 1/4 to 3/4 inch diameter sulfide bearing pellets can be desulfurized in less than thirty minutes at 2100°F and a 5 mole per minute per mole pellet sulfides steam rate.

2. Based on the experimental findings of this study, a suggested process flow sheet has been generated and no unusual equipment or unit operations are required to operate the process.

3. For the suggested process flow sheet, the return on investment for the process under a number of financial situations has been generated. Specifically, for a coal producer using the process selling sulfur at $20/ton it is estimated that a return on investment of 53 percent would be realized for a one MM ton/year-eight percent sulfur coal refuse plant costing $2.3 million. The size of a sulfur recovery plant operating under the above conditions could be reduced to as low as 100,000 tons/year and still yield a no cost operation. Thus the process can be a profitable means of eliminating coal refuse pollution for large quantities of high sulfur coal refuse or it can be a no cost pollution abatement process for small or moderate quantities of coal refuse.

SECTION II

RECOMMENDATIONS

As originally planned, the development of this process should proceed through three phases: a laboratory feasibility study, a pre-pilot plant study, and a demonstration pilot plant. The laboratory feasibility study has been completed and results indicate that the process is a profitable means of reducing coal refuse stockpile pollution. Because of the excellent experimental results and the favorable process economics obtained in the feasibility study, it is highly recommended that the pre-pilot plant study be immediately funded to insure continuity in the project and a rapid solution to the water pollution problem caused by coal refuse stockpiling.

The pre-pilot plant study is recommended to investigate the operation of the shaft reactor so as to provide scale-up data for a pilot plant design and determine those conditions in the shaft reactor which maximize the formation of sulfur. The important process parameters which affect the shaft reactor operation are the temperature profile (temperature in each of the shaft reactor zones), and the steam and air flow rate relative to the pellet retention time. The effects of these process parameters on the shaft reactor offgas composition and the quality of the fired ash pellet product are of primary concern. Maximizing the elemental sulfur content of the shaft reactor offgas will minimize the cost of the sulfur recovery plant thereby reducing operating costs. The quality of the fired ash pellets will directly affect their market value.

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SECTION III

INTRODUCTION

This study involves the laboratory investigation of a process that eliminates water pollution problems arising from the stockpiling of coal refuse. During the preparation of coal, a coal refuse is produced which has a high ash and pyritic content and a low heating value. Presently, coal refuse has no commercial value and is discarded in piles near the coal preparation plant. As rainfall percolates through the piles, conditions become suitable for the formation of acid from the pyrites contained in the coal refuse. Additional products resulting from the interaction of water, air, and pyrites are ferrous and ferric sulfate. These reaction products are dissolved by surface and ground waters and impart ecological and esthetic damage to streams, rivers, and lakes. Consequently, great need exists for a process that will eliminate or minimize such pollution. The process discussed in this report represents a profitable means of recovering elemental sulfur from coal refuse as it is produced or from existing coal refuse piles. Since the process is economically attractive, it should entice communities and coal producers to utilize rather than stockpile coal refuse; thereby minimizing the water pollution caused by coal refuse.

In this process, limestone and coal refuse are ground, pelletized, and preheated prior to entering a high temperature desulfurizing shaft reactor. In this reactor, the pellets proceed in series through a preheat zone, a sulfide formation zone where coal refuse sulfur is converted to sulfides, a desulfurization zone where the pellets are contacted with steam, a gasification zone where coal refuse carbon is burned to supply the shaft heat requirements, and finally a pellet cooling, air preheating zone. The products of the reactor are hard, fired, ash pellets and a hydrogen sulfide-sulfur-sulfur dioxide (H_2S-S-SO_2) bearing offgas. After sulfur, tar, and other gaseous materials are removed from the offgas, the resulting H_2S-SO_2 gaseous mixture is sent to a conventional Claus sulfur recovery plant.

This study was undertaken to determine the feasibility of the process and the technical aspects of the sulfide formation and desulfurization reactions. In addition to engineering studies, experimentation was completed on the formation of sulfides from the coal refuse sulfur and the desulfurization of the sulfide bearing coal refuse pellets. In the first phase of experimentation, the operating conditions necessary to transform the sulfur contained in coal refuse to a sulfide form (either calcium sulfide or ferrous sulfide) were determined. When the transformation to sulfides has been accomplished, desulfurization of the sulfide bearing pellets is possible by a high temperature method in which the pellets are reacted with steam to form calcium and ferrous oxides and hydrogen sulfide. The hydrogen sulfide can then be converted to elemental sulfur using the standard Claus sulfur recovery process.

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Sulfide formation occurs by two reactions. The first is the thermal decomposition of pyrites to ferrous sulfide and sulfur. The reaction is well known and occurs readily at about 1200-1300°F. The second reaction (which produces calcium sulfide) is not fully understood but apparently sulfides are formed by reactions of CaO with sulfur liberated from the pyrite decomposition and/or the volatile organic sulfur. In the sulfide formation study the effects of reaction temperature, limestone content, limestone particle size, limestone type, and residence time on the formation of sulfides were investigated.

The second phase of experimentation concerned the desulfurization of the sulfide bearing coal refuse pellets. As stated previously, steam is reacted with the sulfide bearing pellets to form ferrous and calcium oxides and hydrogen sulfide. However, it was found that the desulfurization offgas also contained elemental sulfur and sulfur dioxide in addition to hydrogen sulfide. It was speculated that sulfur dioxide was being formed by the reaction of H_2S with steam. The presence of elemental sulfur probably results from the high temperature H_2S decomposition to molecular hydrogen and sulfur and/or from the Claus reaction between H_2S and SO_2. The following variables were studied to determine their effects on the desulfurization offgas composition and the rate of desulfurization of the pellet: reaction time, steam rate, reaction temperature, and pellet size. The objective was to determine those operating conditions which maximized the production of sulfur while minimizing the formation of sulfur dioxide. By maximizing the production of sulfur, the size and consequently the cost of the sulfur recovery plant can be minimized.

Based on the experimental results of the study, a process flow chart has been devised and is discussed in a later section. Using this flow chart, the economics of the process were investigated and are also presented.

SECTION IV

RAW MATERIALS USED

Coal refuse was obtained from the Truax-Traer Coal Company of Pickneyville, Illinois. The material was crushed in a jet impact pulverizer to yield a finer sized, homogeneous sample for experimentation. Table 1 presents the screen analysis of the coal refuse.

TABLE 1
COAL REFUSE SCREEN ANALYSIS

U. S. Screen	Percent Weight
+ 40	1.6
-40 + 60	3.3
-60 + 100	6.6
-100 + 200	13.4
-200 + 325	9.5
-325	65.6

The coal refuse was analyzed for its total sulfur content. Several samples were analyzed in an attempt to obtain a representative value for the sulfur content. The following percentages of sulfur in the coal refuse were obtained for the four samples analyzed: 15.1, 15.2, 17.5, and 18.2. An average value of 16 percent sulfur was used for the experimental calculations. The coal refuse was also analyzed for the pyritic and organic sulfur. The method used is described by the American Society of Testing Materials in A.S.T.M. designation D2492-66T. The amounts of pyritic and organic sulfur found were 12.1 and 3.9 percent respectively.

Several different types and particle size distribution limestone samples were prepared for experimentation. The bulk of the experimental work was conducted using limestone obtained from the U. S. Gypsum Company in Bellefonte, Pennsylvania. This limestone contained 97.7 percent $CaCO_3$. Other limestones used were from the Greer Limestone Company of Germany Valley, West Virginia, and the Elkins Limestone Company in Elkins, West Virginia. Their $CaCO_3$ contents were 98.8 percent and 58.75 percent respectively as stated by the manufacturers. Screen analyses and external surface area measurements were conducted on the limestone samples and appear in Tables 2 and 3.

TABLE 2
SCREEN ANALYSIS OF LIMESTONE SAMPLES

U. S. Gypsum Limestone

	Percent Weight			
Screen	Sample As Received	-40 Mesh Sample	-60 Mesh Sample	-100 Mesh Sample
+ 60	15.9	19.9	nil	nil
-60 + 100	78.6	28.9	35.9	nil
-100 + 200	1.2	21.2	26.5	41.4
-200	4.3	30.0	37.6	58.6

TABLE 2 CONTINUED

Elkins Limestone

Screen	Percent Weight Sample As Received	-100 Mesh Samples
+ 20	33.6	nil
-20 + 100	41.6	nil
-100 + 200	3.2	59.2
-200 + 325	0.9	16.7
-325	20.7	24.1

Greer Limestone (Germany Valley)

Screen	Percent Weight Sample As Received	-100 Mesh Samples
+ 20	15.5	nil
-20 + 100	71.3	nil
-100 + 200	9.8	69.1
-200 + 325	2.6	25.4
-325	0.8	5.5

TABLE 3

EXTERNAL SPECIFIC SURFACE AREA OF LIMESTONE SAMPLES

	Surface Area, cm^2/ gram -40 Mesh	-60 Mesh	-100 Mesh
U. S. Gypsum Limestone	910	1603	2161
Elkins Limestone	-	-	1615
Germany Valley Limestone	-	-	1575

The external surface area was determined using an air permeability technique in which the Carman-Kozeny equation was used to relate the external surface area to the pressure drop of air passing through a packed bed of limestone.

SECTION V

EXPERIMENTAL TECHNIQUE AND APPARATUS

Coal refuse pellets were prepared in a laboratory disc pelletizer. Coal refuse, limestone, and water (spray) were continuously fed onto the rotating disc to produce pellets of a desired size. The most important variables in the pelletizing operation were the amount of water added and the disc rotation speed. The speed of the disc must be regulated so that the pellets can roll across as large a portion of the disc face as possible. A maximum amount of rolling is important to make compact, homogeneous pellets. If an excess of water is used, the pellets will cling together resulting in agglomeration and seeding (small pellets clinging to the sides of larger ones). No attempt was made to correlate pelletizing variables since the technology of commercial pelletizers has been developed and no problems are anticipated in the manufacture of coal refuse pellets.

Experimentation was divided into two distinct phases. The first phase entailed reacting the coal refuse-limestone pellets in a high temperature furnace for various times to convert the coal refuse sulfur into sulfide forms (ferrous sulfide and calcium sulfide). The second phase concerned desulfurization experiments aimed at converting the sulfides to hydrogen sulfide and elemental sulfur. The experimental apparatus and methods will now be described.

A high temperature electric tube furnace was used for the sulfide formation experimentation. The furnace was heated by four symmetrically arranged glow bars which surrounded and were parallel to the ceramic reaction tube. The temperature was controlled by two voltage taps located on the side of the furnace. One tap was for a coarse control of temperature and the other was a fine voltage tap capable of changing the furnace temperature by 30-50°F. The ceramic reaction tube was 1-3/4 inches I.D. by 48 inches long.

In the sulfide formation investigation, pre-weighed (± 0.001 gram) pellets were placed in ceramic reaction boats and pushed into the hot zone of the furnace with a long, thin rod. In most instances, two or three pellets were reacted simultaneously. A flow of nitrogen (about 20 standard cubic feet per hour) was maintained before, during, and after the reaction of the pellets. It was discovered that the sulfur contained in the pellets was being oxidized to sulfur dioxide if both ends of the ceramic reaction tube were open to the atmosphere. After the nitrogen purge was installed, no sulfur loss as sulfur dioxide was experienced. After a given period of time, the pellets were pulled from the furnace and placed in an air-tight iron heat sink. The purpose of the heat sink was to cool the pellets, stop the various reactions at the time the pellets were withdrawn from the furnace, and prevent hot pellet oxidation due to contact with air. The pellets were analyzed for their ferrous and calcium sulfide contents. A method for determining the sulfide contents is described in the Appendix.

The second phase of experimentation concerned the desulfurization of sulfide bearing pellets. The desulfurization experiments were conducted at temperatures of 1600-2600°F. A schematic diagram of the desulfurization equipment is shown in Figure 1. The electric tube furnace used for the sulfide formation study was also used for the high temperature desulfurization experiments. Steam was generated in a flask outside the furnace and introduced at one end of a 1-1/2 inch I.D., ceramic lined, Inconel reaction tube. A nitrogen flow was maintained in the furnace countercurrent to the eventual steam flow until steam was introduced into the furnace. A sulfide bearing pellet was placed on a ceramic boat and inserted into the furnace; simultaneously, steam was introduced into the reaction tube and the nitrogen flow was terminated. The excess steam and gaseous products of reaction exiting the reaction tube passed through a water cooled condenser where steam was condensed and the gases cooled. The gases then passed through an absorbing solution of $CuSO_4$ which trapped both SO_2 and H_2S. The gas exiting the absorption solution was bubbled through a solution that became colorless (it was initially blue) if either SO_2 or H_2S was present. There were no instances in which either gas escaped the $CuSO_4$ solution. After a specified reaction time, the steam flow was terminated and the $CuSO_4$ solution analyzed to determine the cumulative amounts of H_2S and SO_2 generated in the experiments. An explanation of these analyses is given in the Appendix. The coal refuse pellet was removed from the furnace, cooled in a heat sink, and analyzed for unreacted sulfides to determine the extent of reaction.

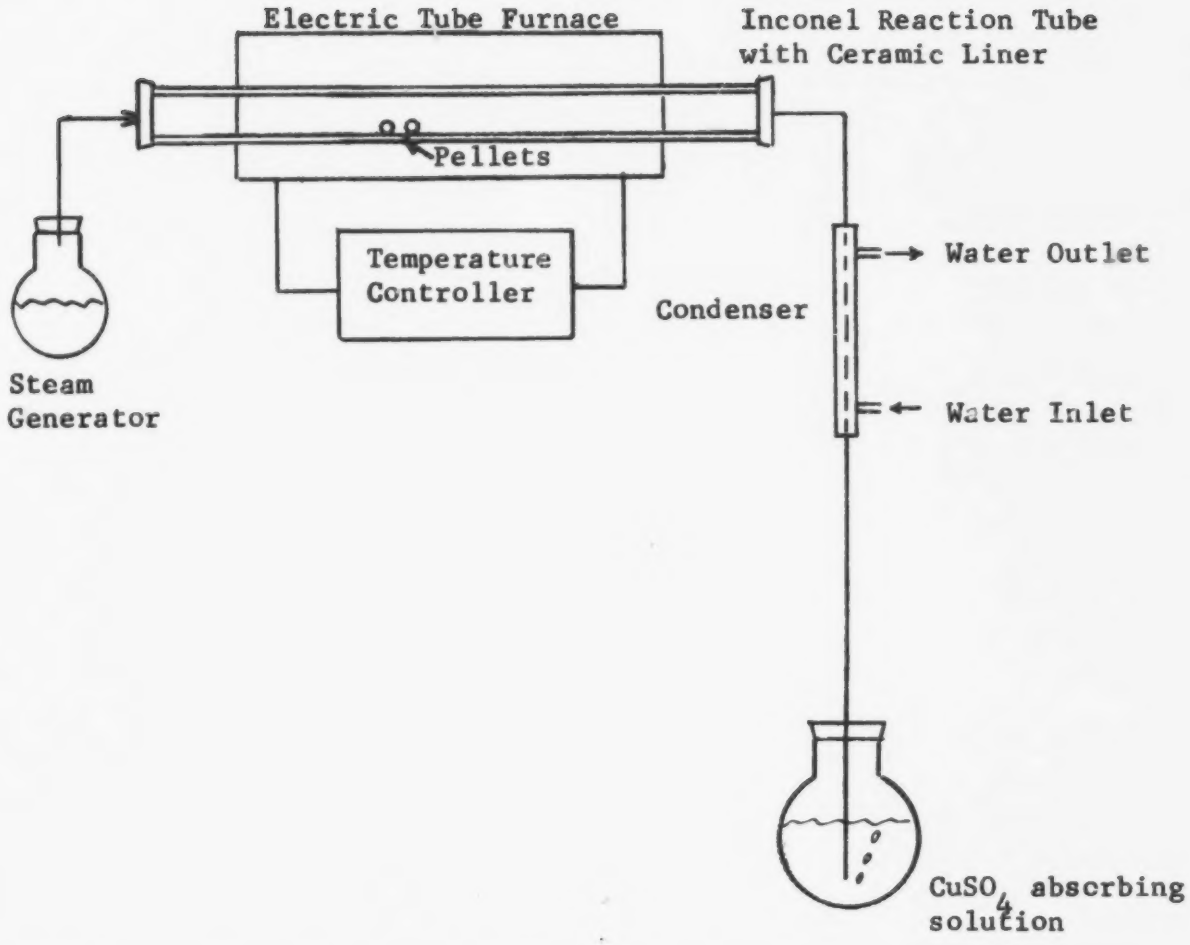

FIGURE 1-EXPERIMENTAL EQUIPMENT FOR HIGH TEMPERATURE DESULFURIZATION

and 65 percent coal refuse were reacted in the tube furnace for times of 5 to 40 minutes. The results are shown in Figure 2 where it is seen that conversion of coal refuse sulfur to sulfides (defined as the moles of sulfur as sulfides in the reacted pellet divided by the moles of sulfur initially present) does not significantly increase after 15 minutes where a maximum conversion of about 0.6 was reached. Based on this finding, all subsequent experimentation was conducted using residence times of 30 minutes.

As previously indicated, pyrites, FeS_2, will decompose to form ferrous sulfide and sulfur. At the reaction temperature used, the sulfur left the pellet in gaseous form. Consequently, due to the manner in which sulfide formation or conversion is defined, a conversion with a value of one cannot be attained since sulfur is leaving as a gas and does not appear as a sulfide. Assuming that the sulfur leaving the pellet results only from the decomposition of pyrites, then the sulfur to sulfide conversion as defined above has a maximum theoretical value of 0.62 for the 16 percent sulfur coal refuse (12.1 percent pyritic, 3.9 percent organic) used in these experiments. The value 0.62 assumes that all the organic sulfur initially present in the pellet reacts with lime to form calcium sulfide. The maximum theoretical conversion (Figure 2) agrees quite well with the maximum conversion obtained by experimentation. This finding supports the theory that calcium sulfide is formed by the reaction of coal refuse organic sulfur with lime. More importantly, it indicates that essentially all of the coal refuse sulfur is either trapped as sulfides for subsequent sulfur recovery or appears as recoverable, gaseous, elemental sulfur.

Effect of Limestone Content

The effect of limestone content on the conversion of coal refuse sulfur to sulfides was determined by reacting pellets of various limestone contents (all minus 60 mesh particle size, U.S. Gypsum) at 1900°F for 30 minutes, and analyzing the reacted pellets for their sulfide content. The percentage of limestone was varied between 25 and 65 percent; the results are presented in Figure 3 where the sulfide conversion is 0.57 for 25 percent limestone and 0.70 for 65 percent limestone in the pellet. The figure also shows the effect of limestone content on conversion for pellets containing limestones of other particle sizes (to be discussed in the next section). It is evident that increasing the limestone content increases the conversion of coal refuse sulfur to a sulfide form.

In Figure 3, sulfur to sulfide conversions higher than the theoretical maximum of 0.62 (based on the assumption that all the sulfur formed from the decomposition of pyrites leaves in elemental form) were realized. This is attributed to the excess limestone (lime) which probably reacted with some of the gaseous sulfur produced from the pyrites.

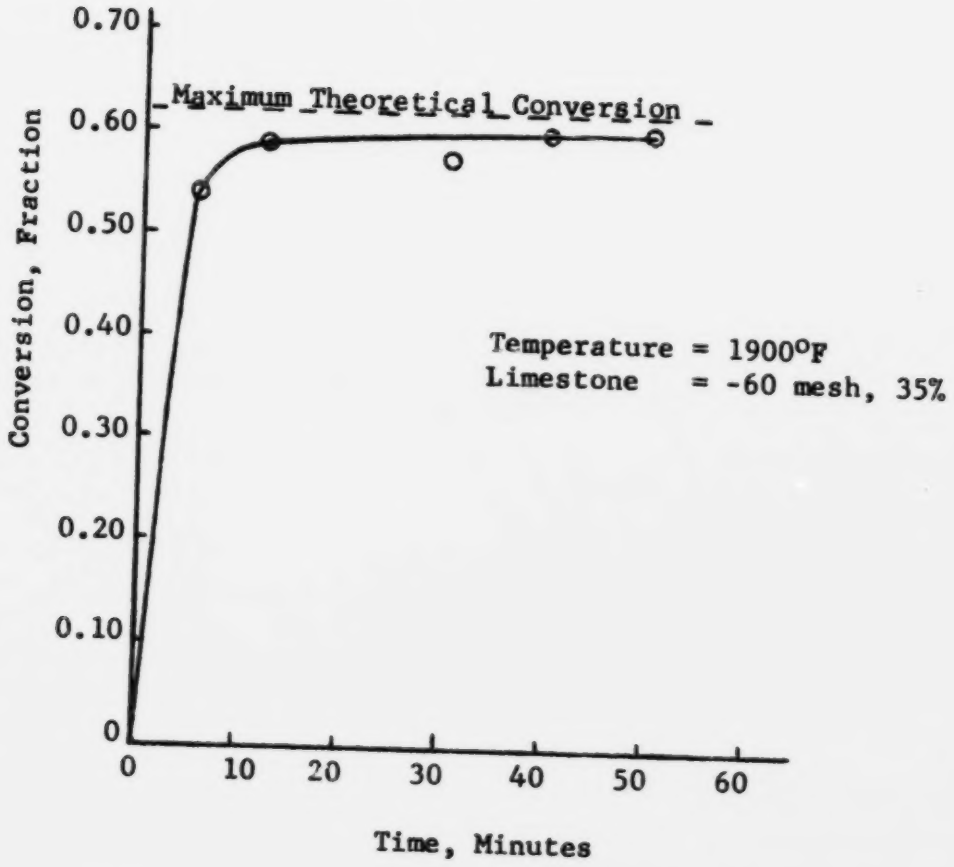

FIGURE 2-EFFECT OF RESIDENCE TIME ON CONVERSION OF COAL REFUSE SULFUR

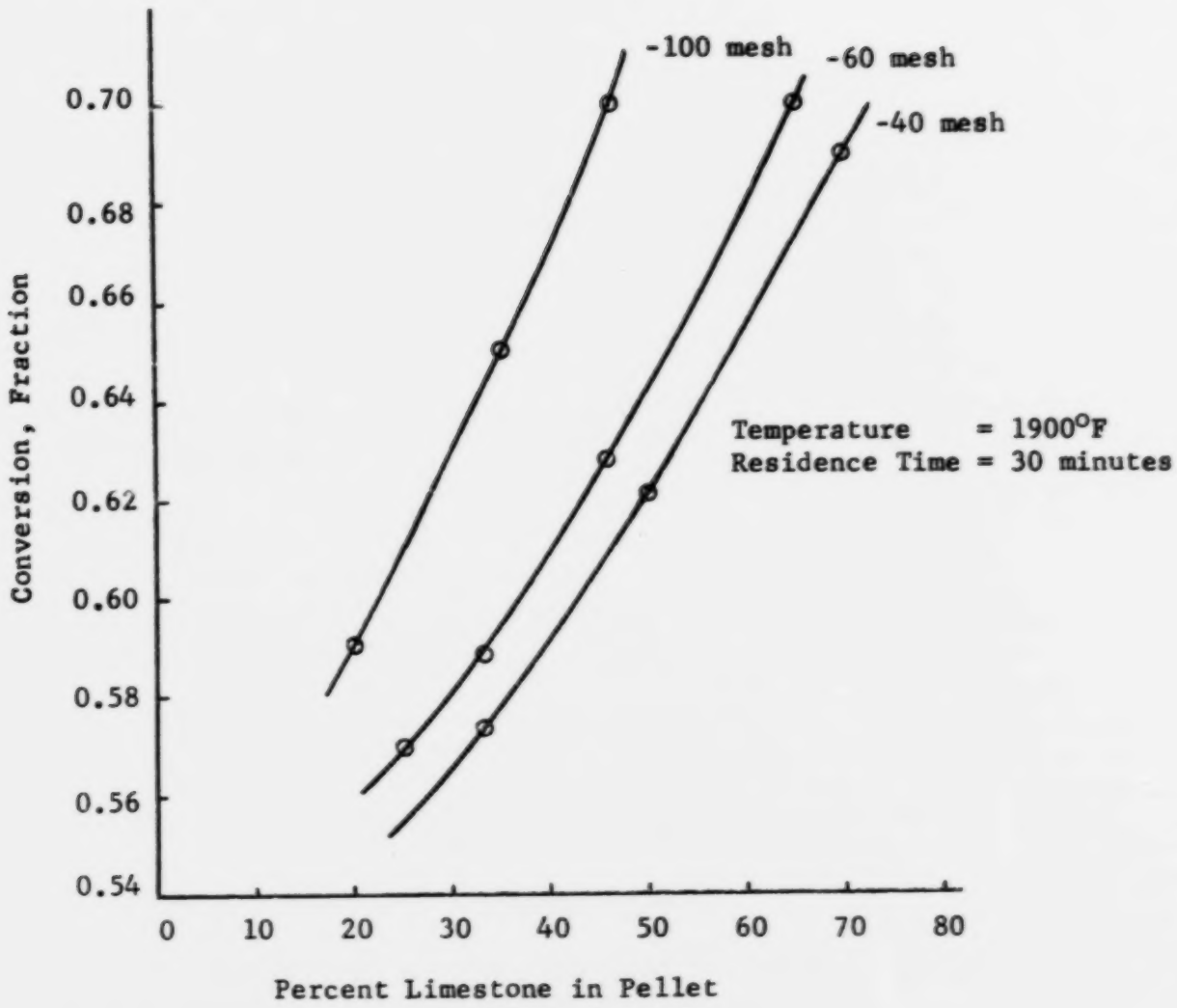

FIGURE 3-EFFECT OF LIMESTONE ON CONVERSION OF COAL REFUSE SULFUR

Effect of Limestone Particle Size

To determine the effect of limestone particle size on the formation of sulfides in coal refuse pellets, pellets were reacted as above using various U.S. Gypsum limestone contents and particle size distributions. Three limestone particle sizes were used, -40 mesh, -60 mesh, and -100 mesh, with external surface areas of 910, 1603, and 2161 cm^2/gram respectively. As was the case in the limestone content study, a reaction temperature of 1900°F, pellet size of one half inch, and a residence time of 30 minutes were used. The results of this study are shown in Figure 3 where it is seen that the limestone particle size has a significant effect upon sulfide formation. For example at a limestone content of 35 percent, the conversion to sulfides is 0.58, 0.59, and 0.65 for -40, -60, and -100 mesh limestone respectively.

For the sulfide formation reactions, the conversion will be related to the external surface area of the lime formed by the decomposition of the U.S. Gypsum limestone. The external surface area of a mass of particles is related to the particle size distribution of these particles. Therefore, while the designation of a -40, or -100 mesh sample will provide a rough, relative comparison of external surface area it is better to consider the external surface area of the limestone to provide data which is more general and adaptable to any particle size. Assuming that the limestone surface area (Table 3) is directly related to the resulting lime surface area, the effect of limestone surface area on sulfide formation at various limestone contents is shown in Figure 4. It is evident from Figure 4 that increasing the external surface area of the U. S. Gypsum limestone at a given limestone content increases the conversion of sulfur to sulfide forms.

Effect of Temperature

To determine the effect of reaction temperature on the formation of sulfides, one half inch pellets were made containing 35 percent limestone (minus 60 mesh) and were reacted for 30 minutes at temperatures ranging from 1760°F to 2500°F. These values were selected because they yielded a sulfur to sulfide conversion approaching the maximum theoretical conversion at 1900°F. The experimental results are presented in Figure 5 where it is seen that the sulfur to sulfide conversion increases as the temperature increases to 1900°F. At this point, the temperature dependence becomes less important and the conversion to sulfides remained essentially constant at about the maximum theoretical conversion as the temperature increased to 2500°F. This infers that temperature has no effect on trapping the gaseous sulfur produced from the decomposition of pyrites as CaS but does affect the quantity of organic sulfur converted to sulfides.

Effect of Different Types of Limestone

As part of the experimental study, it was decided to determine whether limestone mined at different geographical locations and having different chemical analyses had an effect on sulfide formation. Limestones

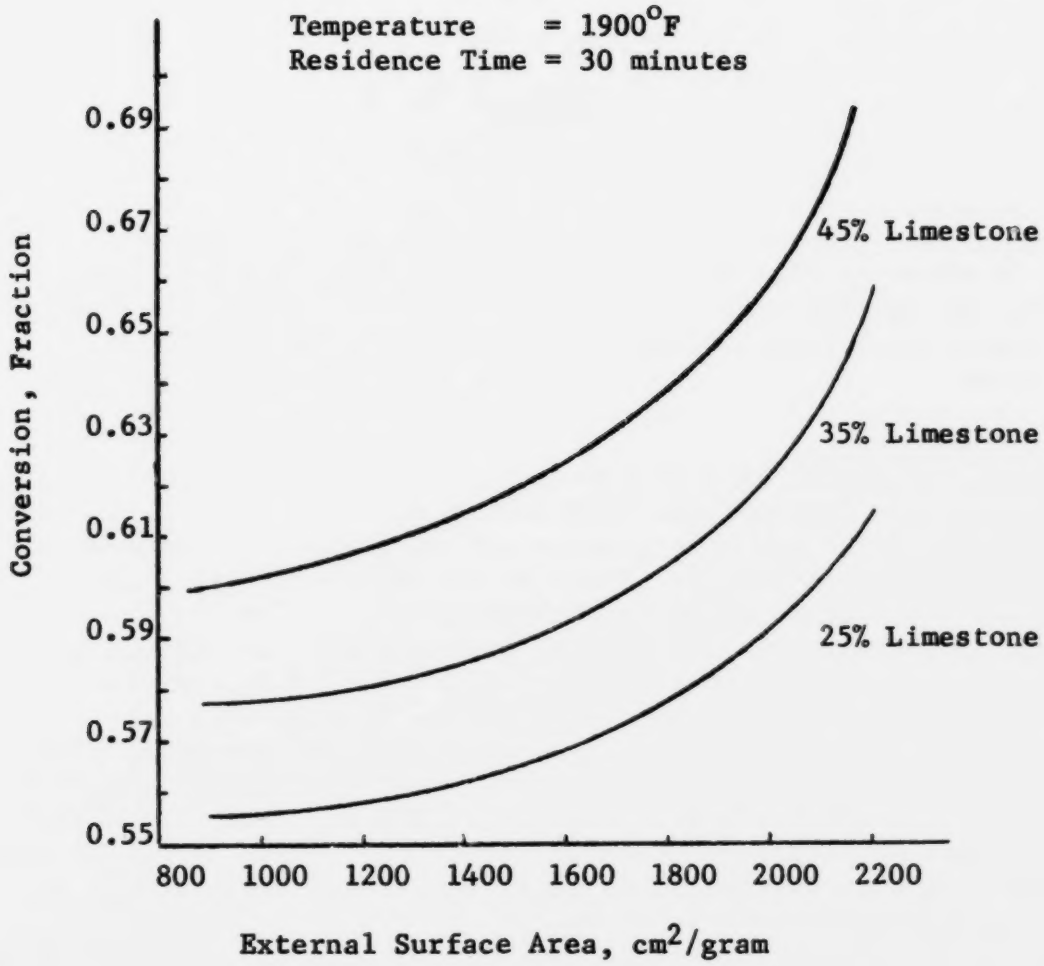

FIGURE 4-EFFECT OF LIMESTONE SURFACE AREA ON CONVERSION OF COAL REFUSE SULFUR

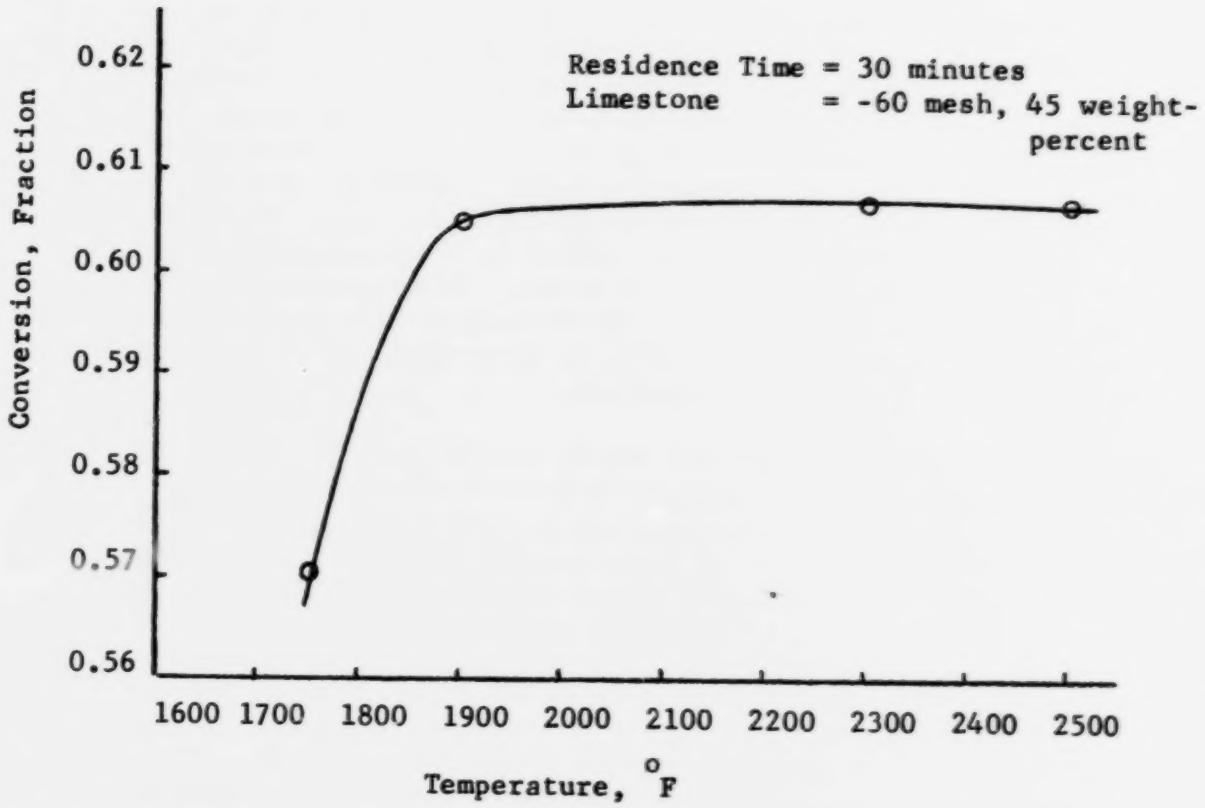

FIGURE 5-EFFECT OF TEMPERATURE ON CONVERSION OF COAL REFUSE SULFUR

obtained from the Elkins Limestone Company and from the Greer Limestone Company were investigated in addition to the U.S. Gypsum Company limestone. The Greer limestone had a high purity (98.8 percent $CaCO_3$) whereas the Elkins limestone had a $CaCO_3$ content of only 58.75 percent. The Elkins limestone is further characterized by having a high percentage of SiO_2 (27.5 percent) compared to 1.2 percent for the Greer limestone. Screen analyses of both limestones on an as received basis and on minus 100 mesh samples appear in Table 2.

Pellets were made from each type of limestone using a minus 100 mesh sample and were formulated so that the ratio of coal refuse to $CaCO_3$ (from the limestone) in the pellet was 65/35. Therefore, the relative amounts of lime to coal refuse were the same in each pellet. The conversion to sulfides was 0.57, 0.62, and 0.64 for Greer, Elkins, and U.S. Gypsum limestones, respectively. Based on these results, it is believed that any type of limestone can be used for sulfide formation provided the proportion used with the coal refuse is adjusted for the $CaCO_3$ content.

Comments

The sulfide formation experimentation has shown that a conservative residence time of 30 minutes will suffice under most operating conditions to yield a maximum conversion of coal refuse sulfur to the sulfide form, and to completely retain the organic sulfur. There is an upper limit to the quantity of limestone (depending on particle size distribution) which should be used so that the gaseous sulfur produced from the decomposition of pyrites is not converted to the sulfide form. Economically it is more attractive to recover this sulfur by condensation rather than desulfurize an increased quantity of sulfides. Experimental results indicate that while the particle size distribution (external surface area) of the limestone is important, the type of limestone has only a minor effect on the extent of sulfide formation.

The results of the sulfide formation study can be used to obtain an estimate of the limestone requirements for coal refuse containing various amounts of sulfur and having various combinations of pyritic and organic sulfur. The effect of temperature on organic sulfur to sulfide conversion is insignificant above 1900°F for residence times of 30 minutes. The quantity of ferrous sulfide produced by pyritic decomposition is not related to the limestone content; consequently, the limestone requirements for complete conversion of organic sulfur to the sulfide form depend on the limestone external surface area and organic sulfur content of the coal refuse. Figure 6 is a plot of limestone area vs. the percent limestone required for sulfide formation at various organic sulfur contents. It was beyond the scope of this feasibility study to investigate coal refuses of different sulfur contents; consequently, the lines shown in Figure 6 for organic sulfur

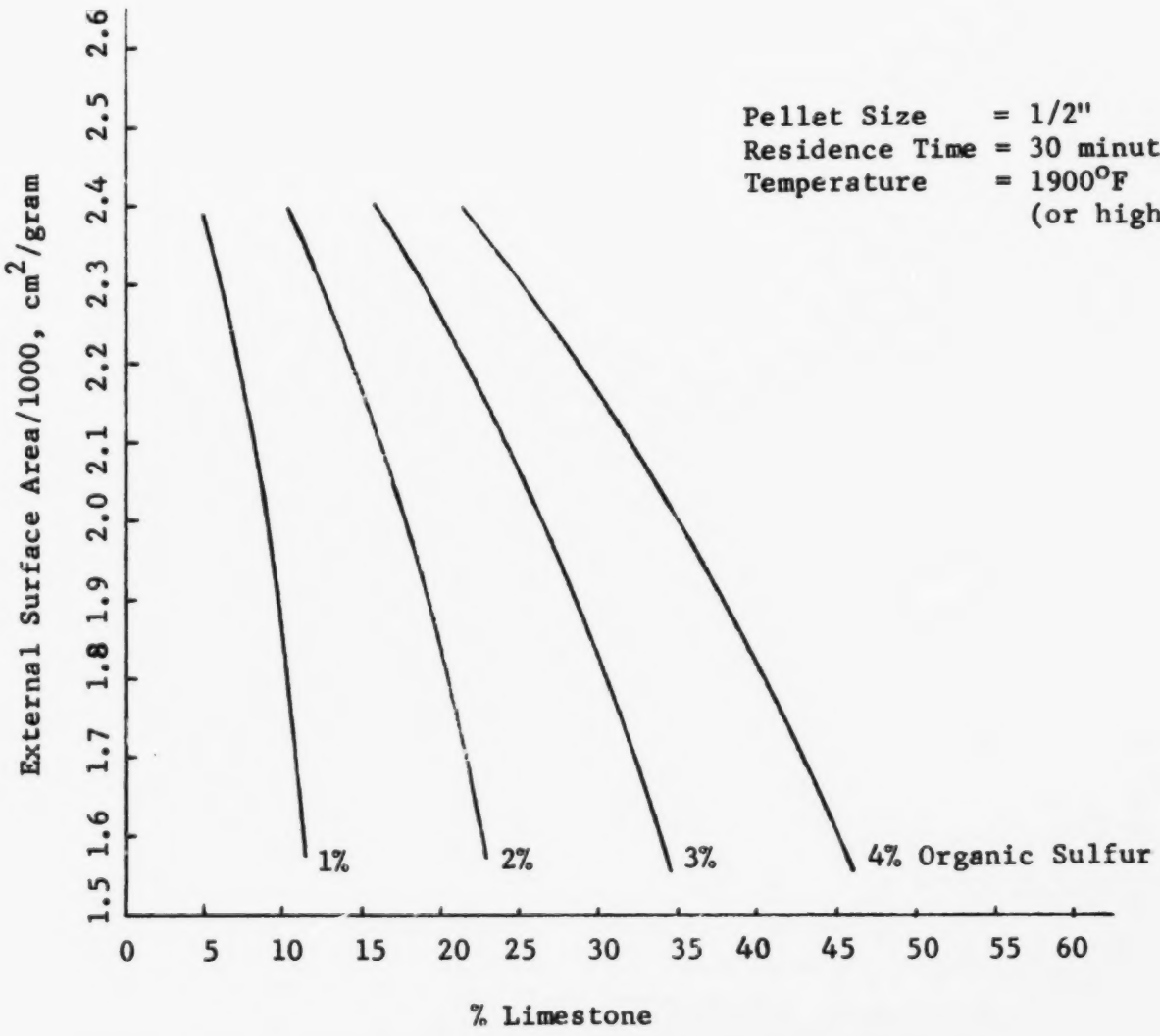
Pellet Size = 1/2"
Residence Time = 30 minutes
Temperature = 1900°F
(or higher)
External Surface Area/1000, cm²/gram
1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6
1%
2%
3%
4% Organic Sulfur
0 5 10 15 20 25 30 35 40 45 50 55 60
% Limestone

FIGURE 6-EFFECT OF ORGANIC SULFUR CONTENT OF COAL REFUSE ON LIMESTONE REQUIREMENTS

contents of one to three percent were prepared assuming a linear relationship between the limestone requirement and organic sulfur content as determined in this study. Figure 6 should be considered only as an estimate of the limestone requirement for sulfide formation when high $CaCO_3$ content limestones are used and can be used for a coal refuse of known organic sulfur content.

SECTION VII

DESULFURIZATION EXPERIMENTATION

Desulfurization

The next phase of experimentation concerned the transformation of the calcium and ferrous sulfides contained in the pellet to hydrogen sulfide. Hydrogen sulfide can then be converted to elemental sulfur using the Claus reaction. Hydrogen sulfide can be produced by reacting the sulfide bearing pellets with steam at temperatures ranging from 1600°F to 2100°F according to the following reactions:

$$FeS + H_2O \longrightarrow FeO + H_2S \quad (5)$$

$$CaS + H_2O \longrightarrow CaO + H_2S \quad (6)$$

The sulfurous offgas from the desulfurization experiments was found to contain sulfur and sulfur dioxide in addition to hydrogen sulfide. It was suspected that sulfur dioxide was being formed by the reaction of steam and hydrogen sulfide (formed via equations 5 and 6) according to the following equation:

$$H_2S + 2H_2O \longrightarrow SO_2 + 3H_2 \quad (7)$$

Elemental sulfur was probably formed by the decomposition of hydrogen sulfide to molecular hydrogen and sulfur at the high temperatures involved:

$$H_2S \longrightarrow H_2 + S \quad (8)$$

The occurrence of this reaction (8) was supported by the fact that hydrogen was detected in the desulfurization offgas. The presence of sulfur in the offgas may also occur by reaction of hydrogen sulfide and sulfur dioxide according to:

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S \quad (9)$$

Equation 9 is the Claus reaction and is catalyzed by alumina which is a component of coal refuse ash.

Preparation of Sulfide Bearing Pellets

The sulfide bearing pellets used for the desulfurization experiments were prepared using 35 percent, -100 mesh U. S. Gypsum Company limestone and 65 percent coal refuse. One half inch diameter coal refuse-limestone pellets were reacted for 30 minutes at 1900°F to yield a 0.62 conversion of the coal refuse sulfur to sulfides. These sulfide bearing pellets were used for all subsequent experimentation except the pellet size study. The parameter studies and their effects on the reaction products and residence time requirements for desulfurization will now be discussed.

Effect of Time on Pellet Sulfide Content

To initiate the desulfurization experimentation, a study was made of the effect of time on the desulfurization of sulfide bearing pellets. Pellets were reacted with steam using the equipment shown in Figure 1 for various times and were analyzed after reaction to determine their unreacted sulfide

content. A reaction temperature of 2100°F and a steam rate of 50 times the stoichiometric requirement was used. In this discussion, the steam rate will be represented as moles of steam contacting the pellet per minute per mole of sulfides originally present in the sulfide bearing pellet. For this experiment, the steam rate was 60 moles per minute per mole of sulfides. The experimental results are shown in Figure 7 where the fraction of unreacted sulfides is plotted versus reaction time.

As seen in Figure 7, after 20 minutes, the coal refuse pellet was completely reacted and contained no sulfur in the form of calcium sulfide or ferrous sulfide. Also, after a period of only five minutes about 86 percent of the initial sulfides had reacted leaving only 14 percent available for further reaction. The results of this experiment indicate that reasonable commercial and experimental residence times could be achieved using 1/2 inch pellets and a reaction temperature of 2100°F.

Effect of Time on Desulfurization Offgas Composition

Experiments to determine the effect of time on the composition of desulfurization gaseous reaction products were conducted in the same manner as above except that after various times the accumulated desulfurization offgas was retained and analyzed for SO_2, H_2S, and sulfur by difference. A steam rate of 60 moles per minute per mole initial pellet sulfides was employed as was a reaction temperature of 2100°F. The results are given in Figure 8 where the mole fraction of H_2S, S, and SO_2 produced is shown as a function of time. From Figure 8, it is seen that between five and fifteen minutes the proportions of the sulfur bearing gases are not significantly affected by time. Between fifteen and twenty minutes the fraction of hydrogen sulfide in the total evolved sulfur bearing gas decreased; however, the fraction of sulfur increased and the fraction of SO_2 remained essentially constant.

As seen in Figure 8, the fractions of H_2S, S, and SO_2 in the accumulated desulfurization offgas were 43, 42, and 15 percent respectively after 20 minutes when desulfurization of the pellet was essentially complete. This result infers that the process is workable since the ratio of H_2S to SO_2 is approximately three. A minimum H_2S/SO_2 ratio of two is required for the Claus sulfur recovery process; therefore, excess SO_2 is not produced in the desulfurization offgas. While the above experimental operating conditions suggest that the process is workable, it would be more advantageous to select operating conditions which yield a maximum of sulfur in the offgas rather than H_2S. This situation would minimize the size of the sulfur recovery plant and reduce operating costs. Therefore, the following studies concerning the effect of steam rate on the extent of desulfurization and the desulfurization offgas composition were undertaken.

Effect of Steam Rate on Pellet Sulfide Content

Using the equipment of Figure 1, the effect of steam rate on the desulfurization of sulfide bearing pellets was investigated for a residence

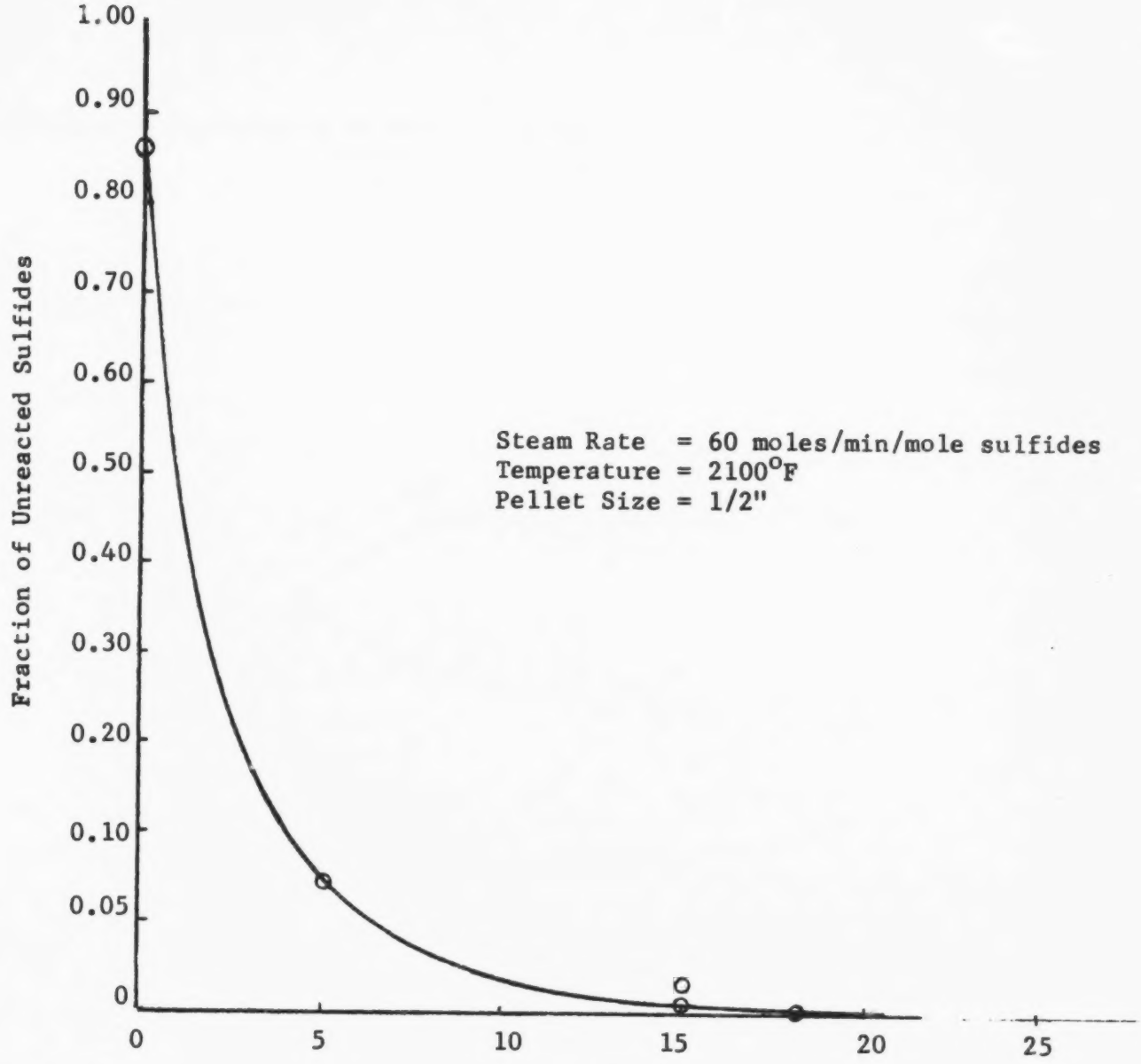

FIGURE 7-EFFECT OF TIME ON FRACTION OF UNREACTED SULFIDES

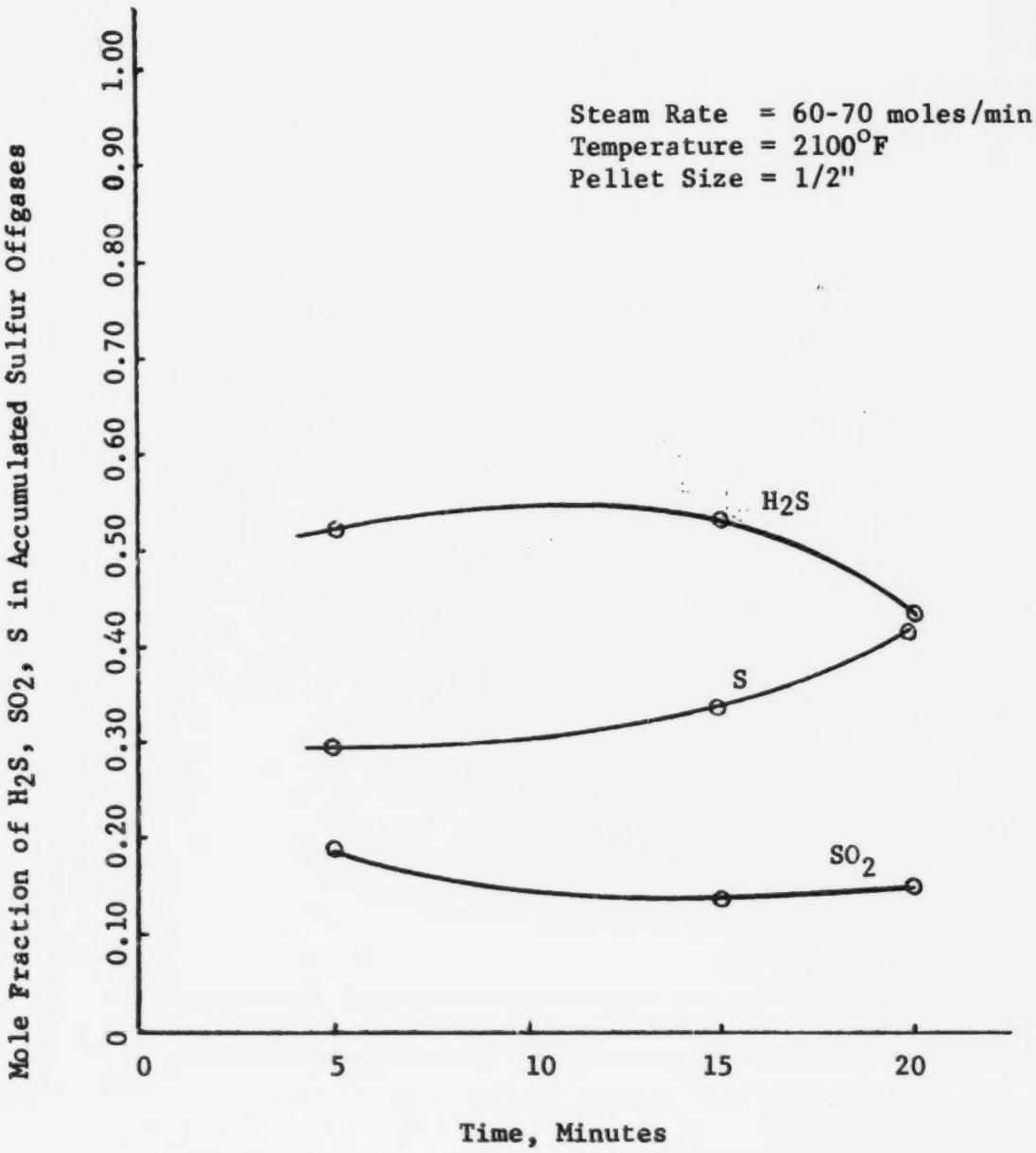

FIGURE 8 EFFECT OF TIME ON REACTION PRODUCTS MIX

time of 30 minutes and a temperature of 2100°F. Several sulfide bearing pellets were individually reacted at various steam rates and analyzed for residual sulfide content. In each case, the amount of steam contacted with the pellet was determined by measuring the amount of water removed from the steam generation flask. The rate was defined as in the previous studies. The results are shown in Figure 9 which is a plot of the fraction of unreacted sulfides in the pellets versus steam rate in the range of 1.6 to 7.2 moles per minute per mole of initial sulfides. Low steam rates were selected for investigation because they are commercially more attractive than high steam rates which would require larger condensers for removal of unreacted steam. They also represent a considerably higher evaporative heat loss if water rather than steam is fed to the desulfurization zone of the shaft reactor.

As seen in Figure 9, the fraction of unreacted sulfides remaining in the pellet after 30 minutes increases as the steam rate is decreased. This is expected since less steam per time is available for the desulfurization reactions (5 and 6):

$$FeS + H_2O \longrightarrow FeO + H_2S \quad (5)$$

$$CaS + H_2O \longrightarrow CaO + H_2S \quad (6)$$

More importantly, the results indicate that at a steam rate of 5 moles per minute per mole of initial sulfides, a residence time of about 30 minutes will be required for desulfurization in the shaft reactor.

While the extent of desulfurization as a function of steam rate is important, the composition of the desulfurization offgas is of prime importance and was the subject of the next investigation.

Effect of Steam Rate on Desulfurization Offgas Composition

The most important concern of the desulfurization study was the effect of various parameters on the composition of the desulfurization offgas because the technical and economic feasibility of the process depends on this composition. In this project, it was determined that the steam rate was the most critical variable affecting the sulfur dioxide, hydrogen sulfide, and elemental sulfur content of the offgas. To ascertain the effect of steam rate on the offgas composition, one half inch sulfide bearing pellets were reacted at 2100°F with steam at various rates. The offgas was collected over a 30 minute period and was subsequently analyzed. Although it was previously determined that a steam rate of about 5 moles per minute per mole initial sulfides at the above operating condition was sufficient to desulfurize the coal refuse pellet in 30 minutes, it was felt that investigation of higher steam rates was justified to observe the effect on offgas composition. Therefore, rates ranging from 1.6 to 32 moles per minute per mole initial sulfides were used. The experimental results appear in Figure 10 and are presented as a plot of the composition of the offgas as a function of steam rate. The important trends observed were that the elemental sulfur

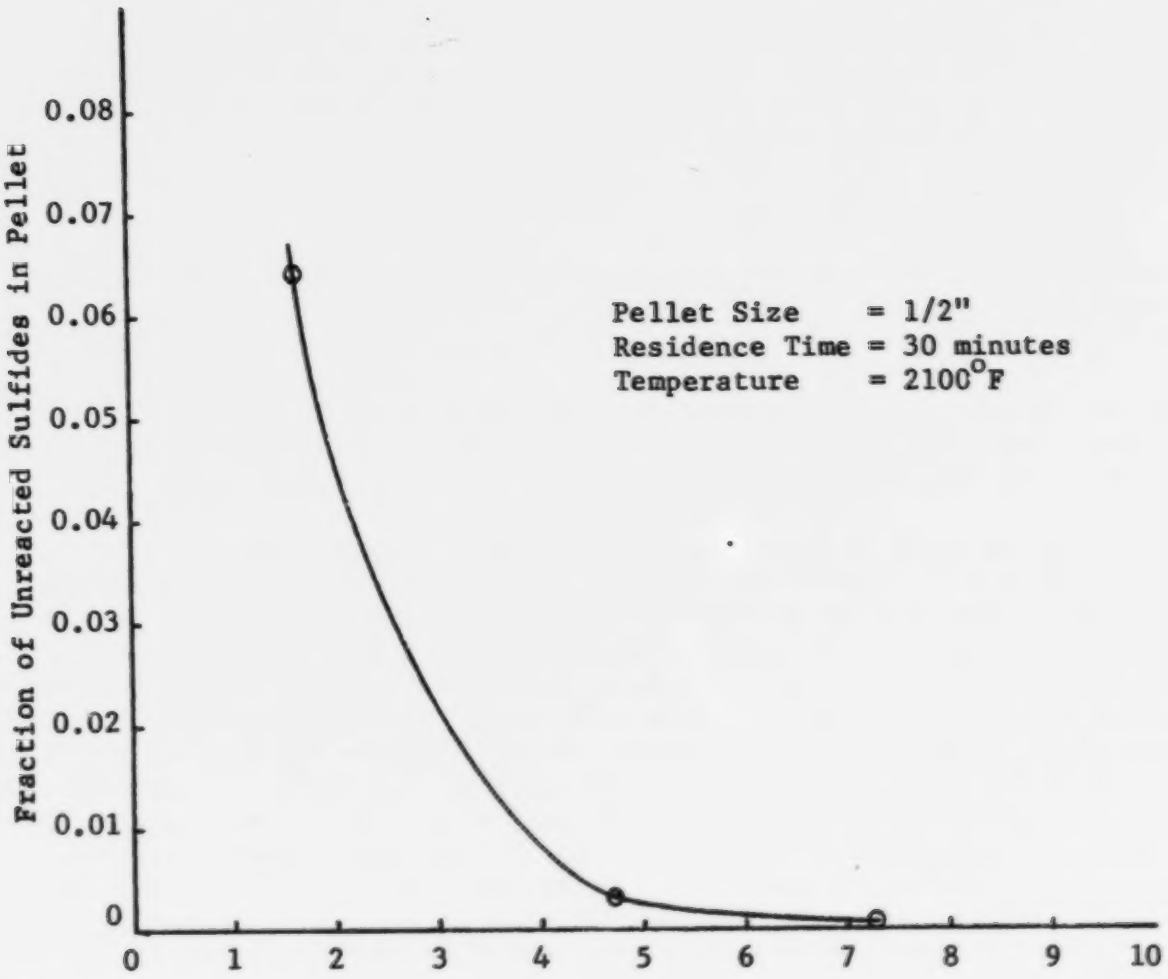

FIGURE 9-EFFECT OF STEAM RATE ON PELLET SULFIDE CONTENT

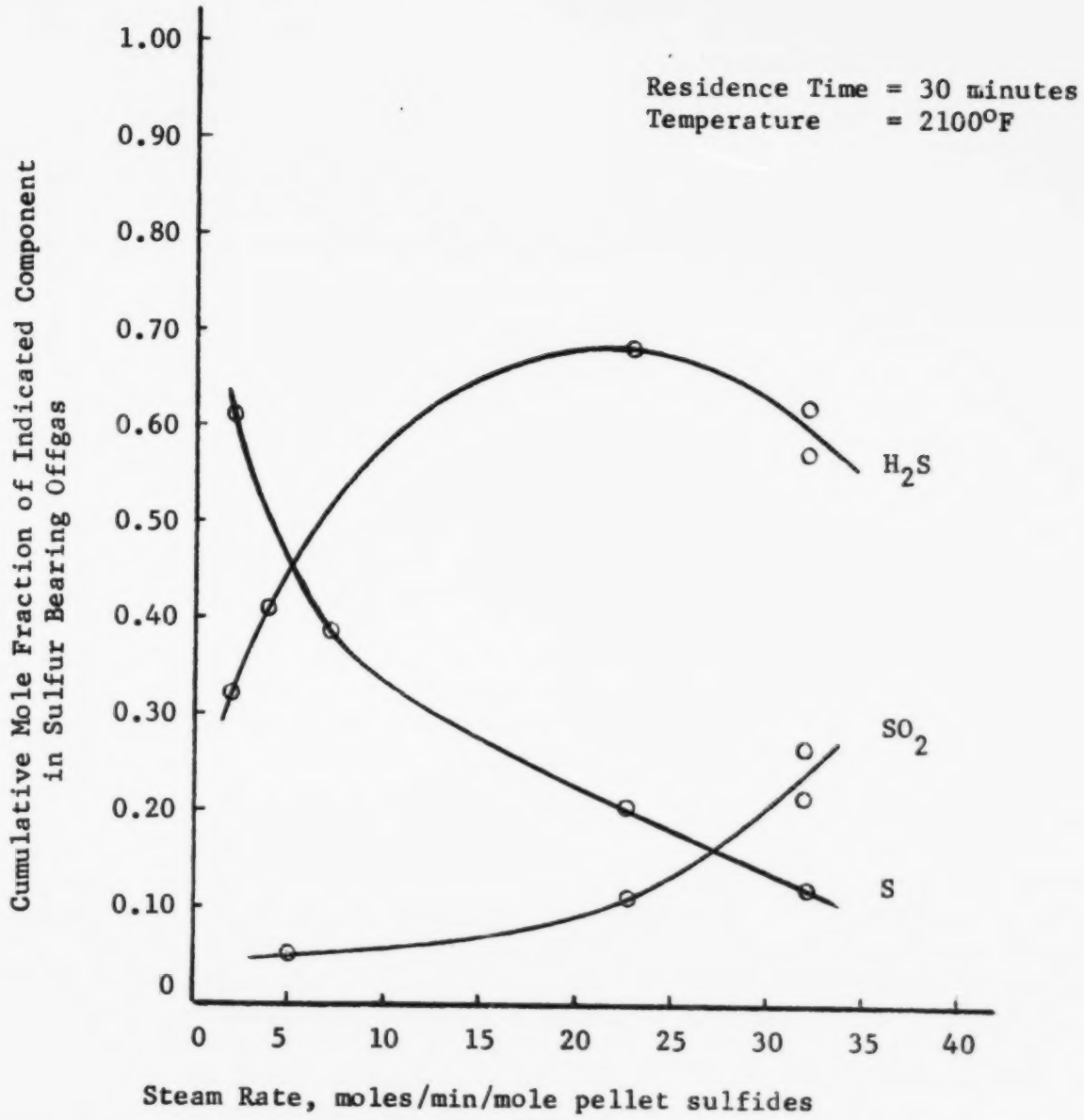

FIGURE 10-EFFECT OF STEAM RATE ON DESULFURIZATION OFFGAS COMPOSITION

content decreased and the sulfur dioxide content increased as the steam rate increased. The fraction of hydrogen sulfide in the offgas increased to a maximum of about 0.68 at a steam rate of 23 moles per minute per mole initial sulfides and then decreased as the steam rate increased to 32.

The reactions that were postulated to occur during desulfurization are reproduced here for convenience:

$$FeS + H_2O \longrightarrow FeO + H_2S \quad (5)$$

$$CaS + H_2O \longrightarrow CaO + H_2S \quad (6)$$

$$H_2S + 2H_2O \longrightarrow SO_2 + 3H_2 \quad (7)$$

$$H_2S \longrightarrow H_2 + 1/2S_2 \quad (8)$$

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S \quad (9)$$

Elemental sulfur is formed via equations (8) and (9). At the high desulfurization temperatures used, it is likely that hydrogen sulfide partially dissociates into its elemental constituents. According to Riesenfeld[2], the extent of dissociation of hydrogen sulfide is 37 and 47 percent at 2192°F and 2372°F, respectively. Reaction (9) probably occurs since this reaction is catalyzed by alumina which is present in the pellet.

Sulfur dioxide is formed according to equation (7) which is the oxidation of hydrogen sulfide by steam. The occurrence of reaction (7) during desulfurization was supported by these facts: decreasing the steam rate decreased the SO_2 content of the offgas, and hydrogen was detected in the offgas.

The important conclusion from Figure 10 is that as low a steam rate as practical should be employed in the process to produce a maximum of sulfur consistent with a reasonable pellet residence time requirement.

The results of this and the prior study indicate that a steam rate of 5 moles per minute per mole of initial sulfides will completely desulfurize the pellet in 30 minutes at 2100°F and yield a desulfurization offgas containing about 45 percent sulfur.

Effect of Temperature on Pellet Sulfide Content

The effect of temperature on the extent of desulfurization of one half inch sulfide bearing pellets was determined by reacting the pellets at various temperatures for 30 minutes at the same steam rate. The steam rate used was 5 moles per minute per mole initial sulfides. After reaction, the pellet was removed from the furnace and analyzed for unreacted sulfides. Figure 11, which is a plot of the fraction of unreacted sulfides in the pellet versus temperature, indicates that the effect of increasing temperature is to reduce the unreacted sulfide content in the pellet. As seen, to achieve complete desulfurization under the above experimental conditions, a temperature of about 1900°F is required. If the temperature is lower, longer pellet residence times will be required. At temperatures greater than 1900°F, it is noted that

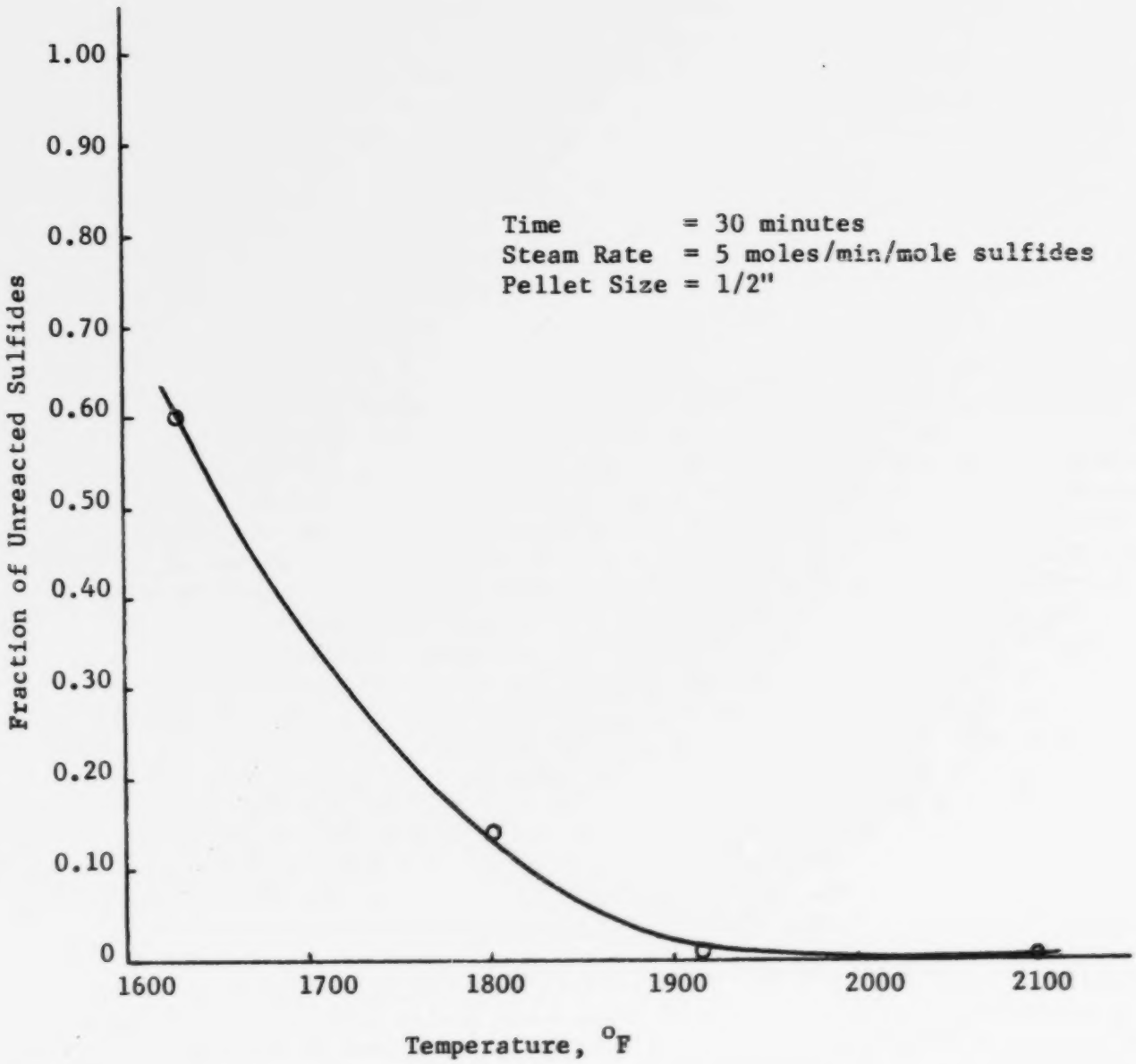

FIGURE 11 -EFFECT OF TEMPERATURE ON FRACTION OF UNREACTED SULFIDES

the pellets were completely desulfurized after 30 minutes. These results indicate that to achieve pellet residence times of 30 minutes or less, a minimum desulfurization temperature of 1900°F is required.

Effect of Temperature on Desulfurization Offgas Composition

The effect of temperature on the desulfurization offgas composition was determined for temperatures ranging from 1900°F to 2100°F. For these experiments, the steam rate was 5 moles per minute per mole initial sulfides and the reaction time was 30 minutes. The desulfurization offgas was collected and analyzed for sulfur dioxide, hydrogen sulfide, and elemental sulfur. Experimental results are presented in Figure 12 which is a plot of the fraction of each constituent in the offgas versus temperature. The hydrogen sulfide content of the offgas does not exhibit temperature dependence to a noticeable extent; however, the sulfur content does as it increased from about 0.40 at 1920°F to 0.49 at 2100°F. Conversely, the sulfur dioxide in the offgas decreased from 0.16 at 1920°F to only 0.06 at 2100°F. These results suggest that higher temperatures result in the production of more sulfur and less sulfur dioxide and should, therefore, be employed in the commercial process.

Effect of Pellet Size on Desulfurization

The final variable studied in the desulfurization phase of experimentation was pellet size and its relation to the residence time required for complete desulfurization. Pellets ranging in size from 1/4 to 3/4 inch were reacted with steam at a rate of 5 moles per minute per mole initial sulfides. The reaction temperature used was 2100°F. These values of temperature and steam rate were chosen because prior experimentation proved them to be the most feasible from the standpoint of application to a commercial process. Several pellets of each size were reacted for times of 5 to 30 minutes to determine the exact residence time required for complete desulfurization. After a specified time, the pellets were withdrawn from the furnace and analyzed for their residual sulfide content. Figure 13 indicates the residence time required to achieve complete desulfurization for each pellet size. As seen, residence times ranged from 12 to 25 minutes for 1/4 to 3/4 inch pellets. The pellet size used in the commercial process will depend on which size is the most economical to manufacture and/or is most marketable; however, each size yielded desulfurization residence times less than 30 minutes at the operating conditions specified above.

Comments

Desulfurization experimentation has shown that 1/4 to 3/4 inch diameter sulfide bearing pellets can be desulfurized in less than 30 minutes at 2100°F and at a 5 moles per minute per mole pellet sulfides steam rate. This steam rate and operating temperature is commercially feasible; consequently, a reasonable shaft reactor residence time is expected. It was found that the effect of decreasing the steam rate is to increase the gaseous elemental sulfur and to decrease the sulfur dioxide formed. It would be advantageous in a commercial unit to produce as much elemental sulfur

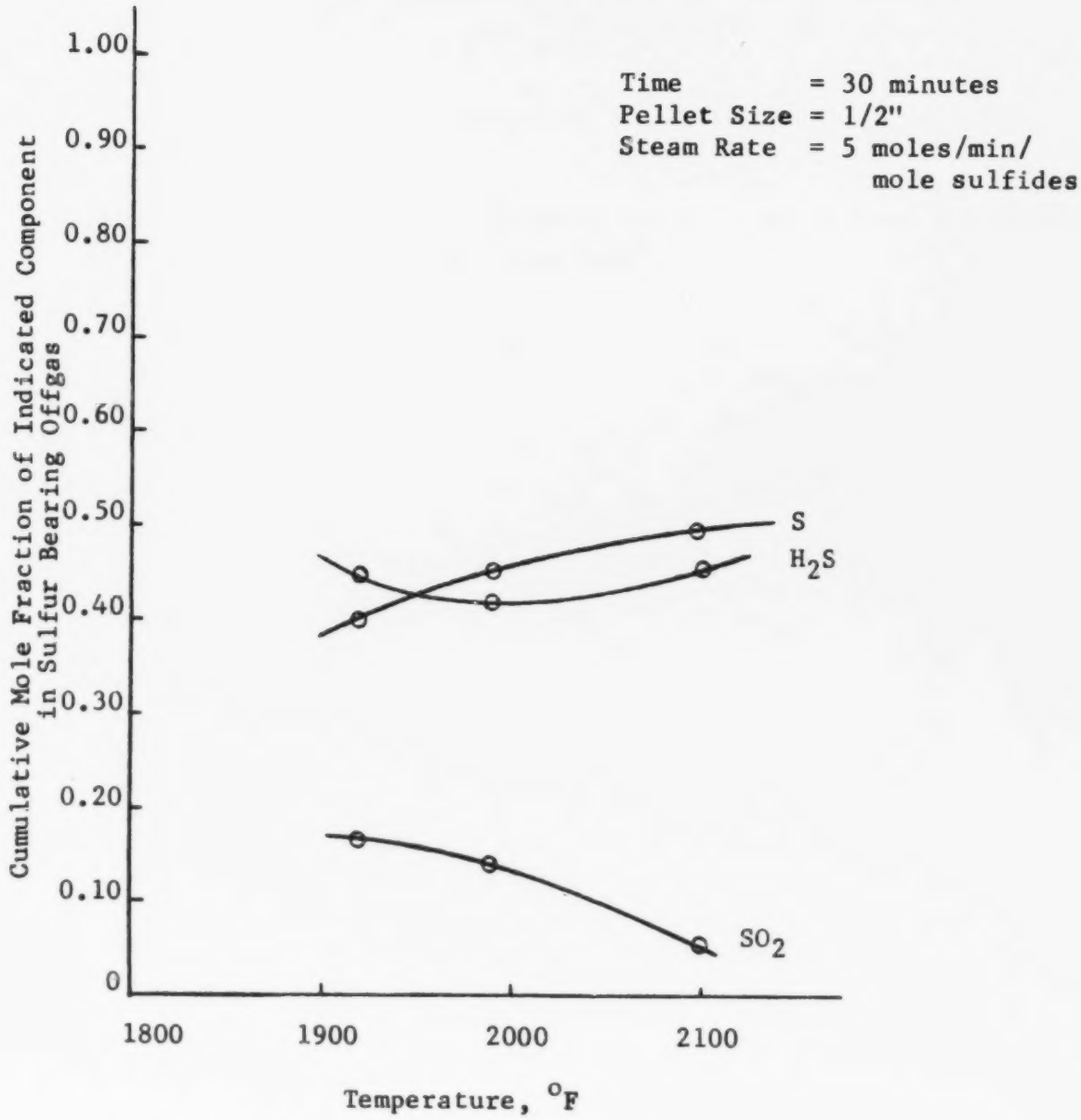

FIGURE 12-EFFECT OF TEMPERATURE ON REACTION PRODUCTS MIX

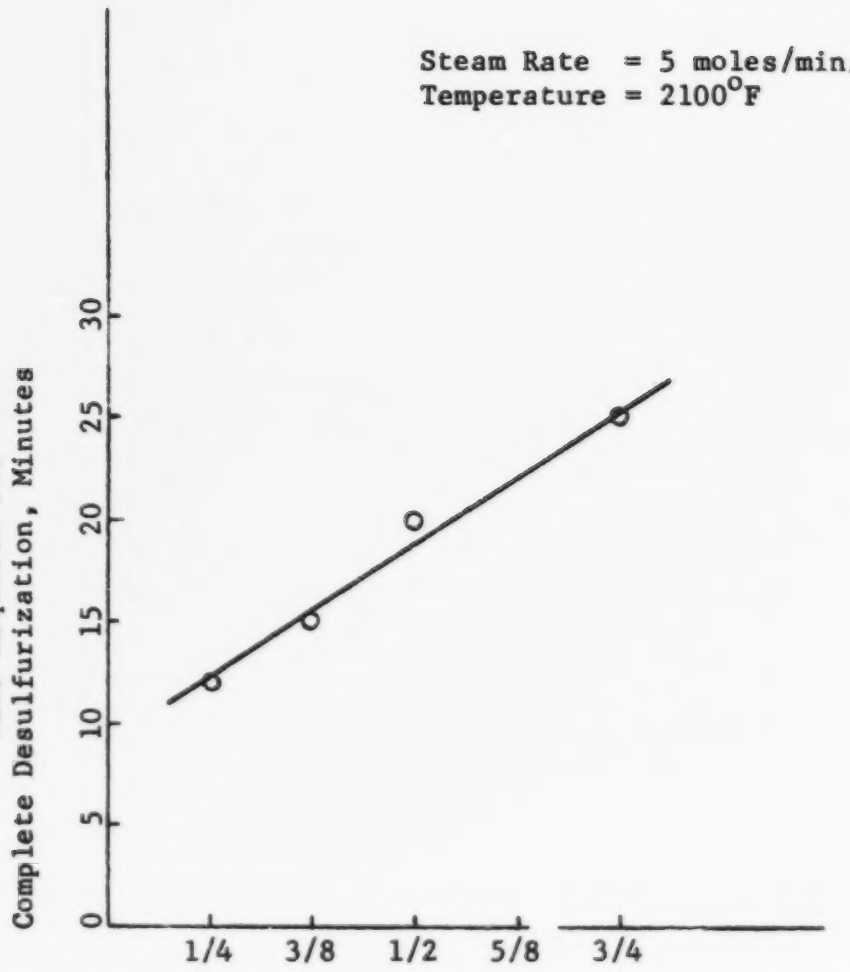

FIGURE 13-RESIDENCE TIME REQUIREMENTS TO ACHIEVE COMPLETE DESULFURIZATION

as possible since the sulfur exiting the reactor can be easily and economically recovered by condensation. The conversion of hydrogen sulfide to sulfur requires a Claus sulfur recovery plant. If the quantity of hydrogen sulfide is reduced, the Claus plant can be smaller thereby enhancing the economics of the process. Therefore, as low a steam rate as possible should be used for desulfurization consistent with residence times of about 30 minutes.

Since pellets ranging in size from 1/4 to 3/4 inch were completely desulfurized in less than 30 minutes at a temperature of 2100°F and a steam rate of 5 moles per minute per mole pellet sulfides, the pellet size(s) to use in the process will depend on which size ash pellet is the most marketable.

SECTION VIII

PROCESS DESCRIPTION

Process Flow Sheet

Bench scale laboratory results indicate that a commercial process can be conceived for the recovery of sulfur from coal refuse. One possible process flow sheet is presented in Figure 14. Limestone and coal refuse from an existing pile or directly from a coal preparation plant are crushed simultaneously in a crusher. The crusher reduces these components to a fine product and provides intimate mixing. The mixture proceeds to a disc pelletizer where pellets are formed and sent to a preheater in which their temperature is raised to 900 -- 1100°F prior to entering a shaft reactor. The energy requirement for preheating is supplied by burning a carbon monoxide-bearing offgas from the H_2S-SO_2 absorption-scrubbing system. The pellet preheater offgas enters a wet scrubbing system where a tar-coal refuse dust mixture is separated from the offgas. In the shaft reactor, sulfur is removed from the preheated pellets by reaction with steam. As the desulfurized pellet travels down through the shaft reactor, air is introduced counter-currently into the shaft to combust the carbon contained within the desulfurized pellet. The heat of combustion not only produces a hard, fired pellet suitable for use as road aggregate, but also produces a hot reducing gas. This reducing gas, as it travels up the shaft reactor, raises the temperature of the preheated pellets so that steam desulfurization occurs. The fired ash pellets are removed and sent to storage for sale. The shaft reactor offgas which contains tars, sulfur, hydrogen sulfide, sulfur dioxide, nitrogen, water, carbon monoxide, and carbon dioxide proceeds to the sulfur-tar recovery system where sulfur and tar are removed from the gaseous stream. The resulting H_2S-SO_2-CO_2-N_2-H_2O gas mixture is sent to a H_2S-SO_2 absorption scrubbing system where the gaseous components are separated. The H_2S-SO_2 gas enters a conventional Claus sulfur recovery plant. In the sulfur recovery plant, steam is generated which can be used in the shaft reactor. The CO-CO_2-N_2 gas from the H_2S-SO_2 absorption scrubbing system proceeds to the pellet preheater where it is burned to supply the energy requirements for preheating.

Operating Technology and Suggested Operating Parameters

The crushing and pelletizing operations are standard and require no further elaboration as to their operation. Crushing and pelletizing are required to minimize dust during subsequent operations, to provide maximum contact between the limestone and coal refuse, and to yield an ash pellet suitable for use as a road aggregate. The pellet preheater may be a direct fired, refractory lined, continuous flow shaft furnace or rotary kiln. The purpose of preheating the pellets prior to entering the shaft reactor is to prevent the sulfur contained in the shaft reactor gas from condensing on the surface of the incoming pellets. If sulfur were to condense on the pellet surface and be carried into the shaft reactor, it would be converted to H_2S and/or SO_2. While this would not affect the overall recovery of sulfur, it would

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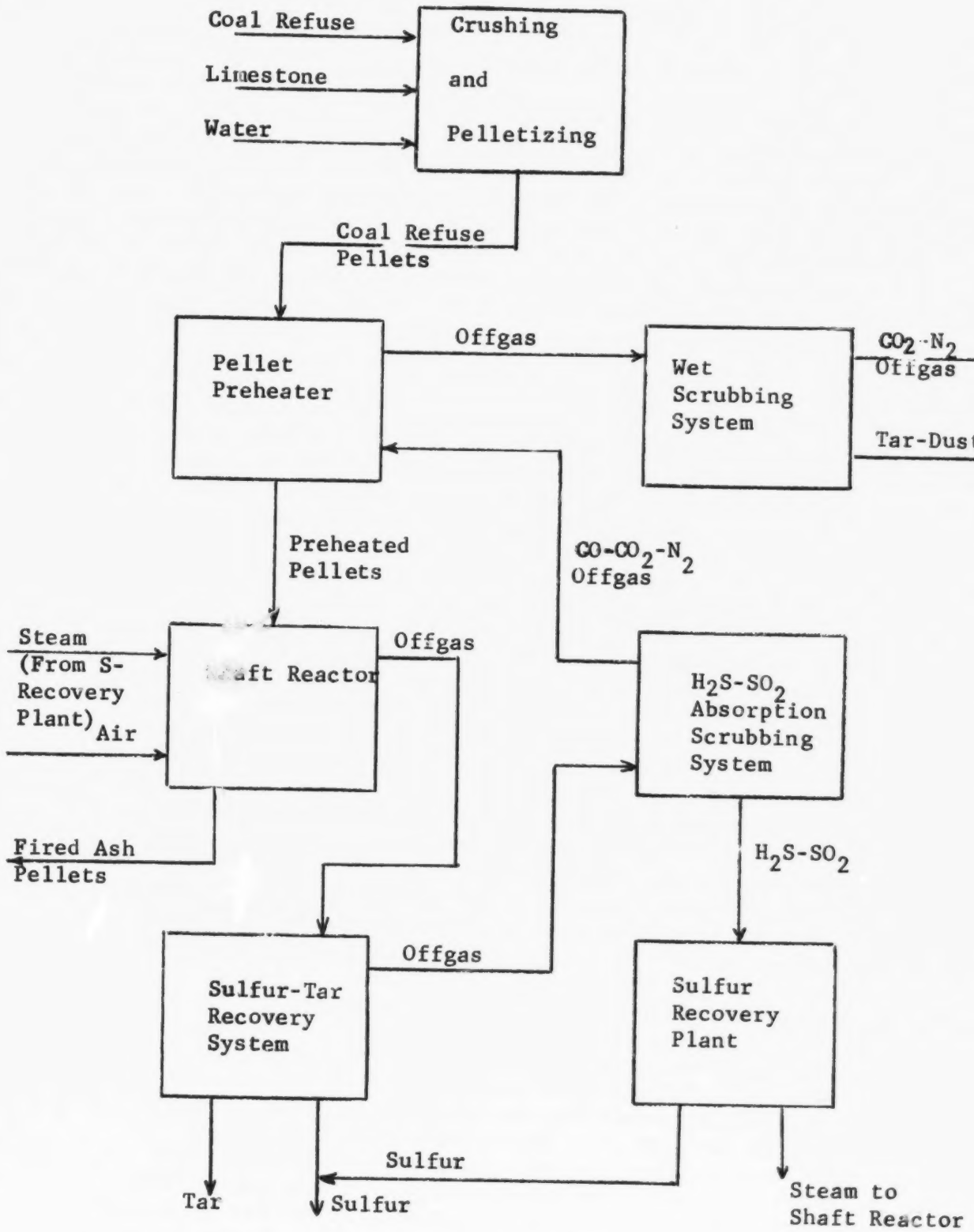

Sulfur Recovery from Coal Refuse

FIGURE 14-PROCESS FLOW CHART

increase the size and cost of the sulfur recovery plant since a higher throughput of the H_2S-SO_2 feed gas would result. The wet scrubbing system consists of a standard scrubber using a closed-loop water scrubbing system. The tars and dust are separated from the water using conventional techniques.

A schematic diagram of the reaction zones of the continuous flow shaft reactor is shown in Figure 15. As seen, the preheated coal refuse pellets entering the shaft reactor proceed in series through five zones (pellet preheating, sulfide formation, desulfurization, gasification, and air preheater) and exit as fired ash pellets.

The reactions occurring in the pellet preheating and sulfide formation zones of the shaft reactor are identical to the ones studied in the sulfide formation phase of the laboratory study; the only significant difference being that the laboratory study used an inert gas whereas in the shaft reactor a highly reducing gas would pass through the pellets. Laboratory results indicate that the amount and particle size of limestone used in the coal refuse pellets be such that the conversion of coal refuse sulfur to sulfides be 0.60-0.65. This can be achieved using 35 percent limestone (-100 mesh) and 65 percent of a 16 percent sulfur coal refuse in the pellet. Of course for lower sulfur content coal refuse, the fraction of limestone would be reduced.

The resulting products of the pellet preheating and sulfide formation zones are FeS-CaS bearing coal refuse pellets which proceed to the desulfurization zone and an offgas containing tars, sulfur, hydrogen sulfide, sulfur dioxide, nitrogen, water, carbon monoxide, and carbon dioxide. The pellets at this point will still contain carbon but be essentially free of volatiles, these volatiles having been removed in the previous two zones.

The same reactions occur in the desulfurization zone that occurred in the pellets during the laboratory investigation of desulfurization. Again, the only difference from the laboratory study is that a highly reducing gas from the gasification zone passes through the pellets. The presence of a highly reducing gas will be beneficial to the process because it will tend to minimize or prevent the formation of sulfur dioxide.

Based on the results of the laboratory study, a low steam rate should be used for desulfurization consistent with complete desulfurization in about 30 minutes. In the laboratory study, a rate of 5 moles per minute per mole initial sulfides was found to accomplish complete desulfurization in less than 30 minutes for pellets up to 3/4 inch diameter. As pointed out in the laboratory study, a low steam rate maximizes production of sulfur and minimizes the formation of SO_2. Temperatures in the range of 1900°F-2100°F should be used in the desulfurization zone since the rate of the desulfurization reaction between steam and sulfides increases with temperature.

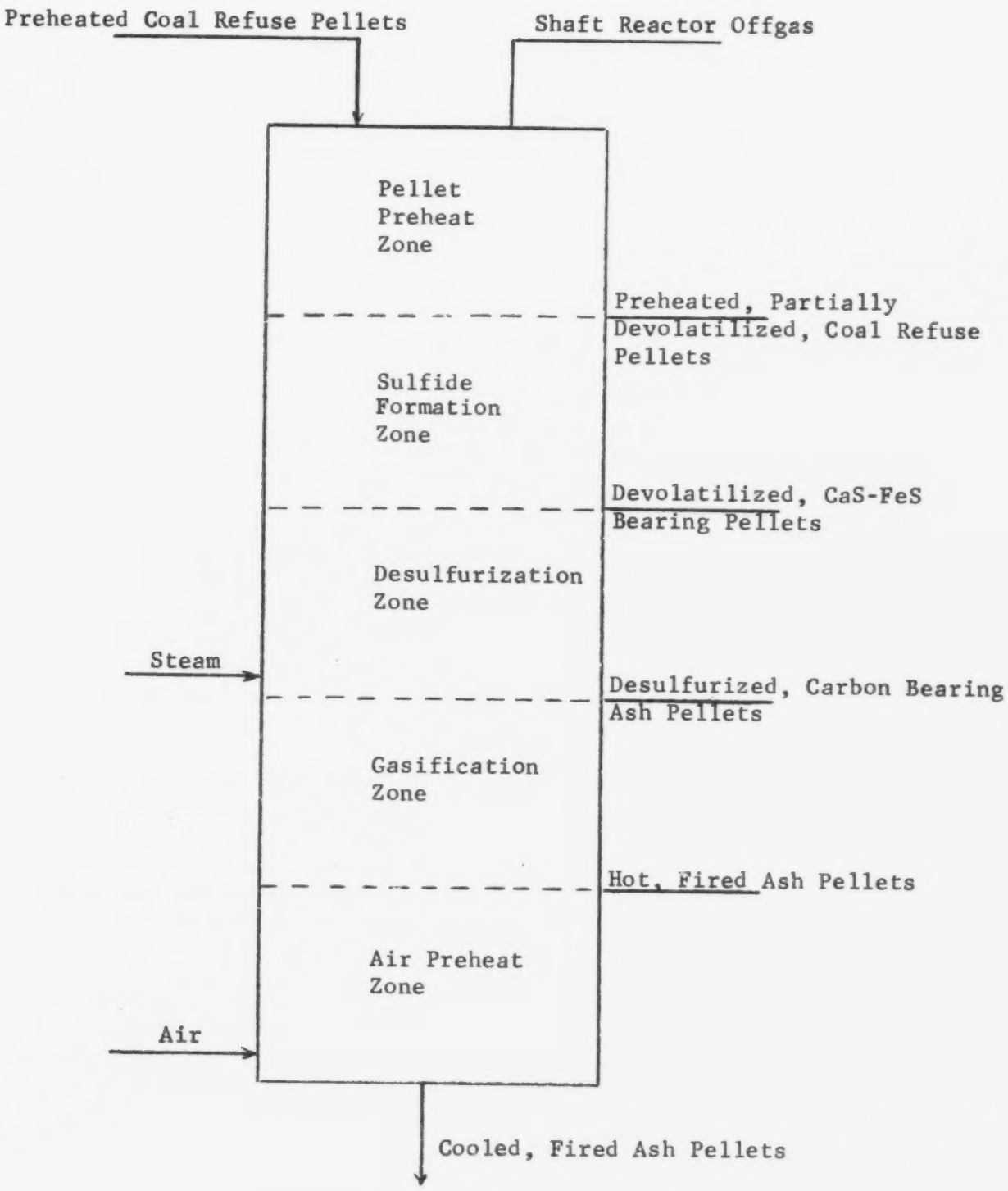

FIGURE 15-SHAFT REACTOR ZONES

The pellets exiting the desulfurization zone will be essentially free of sulfur in any form, completely devolatilized, and will contain carbon and ash constituents. These desulfurized carbon bearing ash pellets then enter the gasification zone. In the gasification zone, the carbon contained in the pellets is reacted with air from the air preheat zone to provide a hot carbon monoxide rich offgas, which supplies the energy requirements of the desulfurization and sulfide formation reactions. The carbon monoxide also provides a reducing atmosphere in which the above operations are carried out, thereby minimizing the formation of sulfur dioxide. In addition, the carbon monoxide is recovered later in the process and is burned to provide the pellet preheating energy requirements. Any sulfur remaining in the desulfurized pellets will be burned to sulfur dioxide to produce sulfur-free fired ash pellets. The air preheat zone serves two purposes. The fired ash pellets from the gasification zone will be used to preheat the incoming air to minimize the energy requirements of the reactor, and will serve to cool the fired ash pellets for ease in removal from the shaft reactor. The experimental results of the laboratory study have shown that both the sulfide formation and desulfurization zone require a maximum of one-half hour pellet residence time. Since the gasification reaction is rapid, the residence time requirement for the desulfurization of the pellets in the shaft reactor will be in the order of two hours--one half hour pellet preheating, one half hour sulfide formation, one half hour desulfurization, and one half hour for gasification and air preheating.

Several possibilities exist for the design of the sulfur-tar recovery system. These include (1) a staged condenser operation in which high-boiling-point organics, sulfur, and tars are separately recovered in sequence, (2) a tank in which the offgas is directly contacted with water producing a floating tar layer and a suspension of sulfur which can be recovered by filtration, or (3) by sulfur scrubbing of the offgas to remove the tar with subsequent condensation of the scrubbed sulfur vapor in a condenser.

The H_2S-SO_2 absorption-scrubbing system will require standard absorption scrubbing equipment. The sulfur-tar recovery system offgas will contain H_2S, SO_2, CO, CO_2, and N_2. One possible scheme is to remove the H_2S-SO_2 and CO_2 using water or ammonia as the absorption reagent. The CO-N_2 offgas would then be used for pellet preheating. The CO_2 content of the H_2S-SO_2-CO_2 mixture could then be removed using propylene carbonate as the absorption reagent to yield an H_2S-SO_2 gaseous feed for the sulfur recovery plant.

The above suggested operating parameters and process flow chart should be considered only as one of many possible alternatives.

SECTION IX

ECONOMIC EVALUATION

Estimated Fixed Capital Investment

Based upon a one million ton per year coal refuse plant (process flow chart--Figure 14) the daily material input and output of the streams of economic significance for an eight percent coal refuse is shown in Table 4. The composition of the coal refuse (dry basis) was assumed to be six percent pyritic and two percent organic sulfur, 40 percent ash, and 45 percent volatile matter and carbon. The results of Table 4 were based on a process requiring the addition of 20 percent by weight limestone to the eight percent coal refuse. According to Figure 6, the limestone requirement will be 20 percent for a coal refuse containing two percent organic sulfur if the limestone external surface area is about 1800-1900 cm^2/gram. In the discussion which follows, the coal refuse sulfur content is assumed present as pyrite and organic sulfur in a 3:1 ratio. The iron remaining in the ash pellets was assumed to be in the form of FeO. From Table 4, the quantity of sulfur produced will be 211 tons/day assuming a 95 percent overall recovery and the production rate of ash pellets will be 1824 tons/day.

TABLE 4
RAW MATERIAL INPUTS AND PRODUCTS
(1MM Ton/Year Coal Refuse Plant)

Inputs	Tons/Day
Coal Refuse (Dry)	2778
Limestone	695
Outputs	
Sulfur (95% Recovery)	211
Fired Ash Pellets (Ash-FeO-CaO)	1824

For a one million ton per year coal refuse plant using a three percent moisture coal refuse, the crusher will handle 2850 tons/day of coal refuse plus 695 tons/day of limestone. The pelletizer is sized to produce approximately 3600 tons/day of pellets depending upon the moisture content of the coal refuse pellet. The pellet preheater is sized to accommodate about 3600 tons/day of pellets. If all the water and 20 percent of the total volatile matter and carbon contained in the coal refuse is driven off in the pellet preheater then the shaft reactor must accommodate about 3000 tons/day of pellets.

Experimental laboratory results indicate that approximately 40 percent of the original sulfur contained in the coal refuse can be converted to sulfur prior to the sulfur recovery plant. Thus, the sulfur recovery plant is sized to yield 125 tons/day of sulfur.

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Based upon the tonnage requirements as specified above, and assuming a two hour residence time requirement for the shaft reactor, the estimated fixed capital required for a plant using one million tons per year of coal refuse is shown in Table 5. As indicated, the fixed capital investment will be $2.3 million for a one MM ton/year coal refuse plant. Black, Sivalls & Bryson constructs sulfur recovery plants; therefore, the estimated capital expenditure for the sulfur recovery plant was based on internal sources. By scaling the equipment costs of Table 5, the capital investment for plants of various capacities and coal refuse sulfur contents were determined and are shown in Figure 16.

TABLE 5
ESTIMATED FIXED CAPITAL FOR A ONE MM TON/YEAR COAL REFUSE PLANT

	(thousands of dollars)
Land & Building	30
Crusher-Pelletizer	100
Pellet Preheater	40
Shaft Reactor	200
Bucket Elevators - Belt Conveyors - Pumps	100
Wet Scrubbing System	20
Sulfur-Tar Recovery System	35
H_2S-SO_2 Scrubbing System	35
1. Total Purchased Equipment	560
Installation, Piping, Electrical Instrumentation, Utilities (85% of 1)	476
2. Physical Plant Costs	1,036
Engineering & Construction (30% of 2)	311
3. Direct Plant Cost	1,347
Contractors Fee & Contingency (20% of 3)	269
	1,616
4. Installed Sulfur Recovery Plant	700
TOTAL FIXED CAPITAL	2,316

Operating Revenue

The daily operating revenue for a one million ton per year coal refuse plant is shown in Table 6 for an eight percent sulfur coal refuse. The

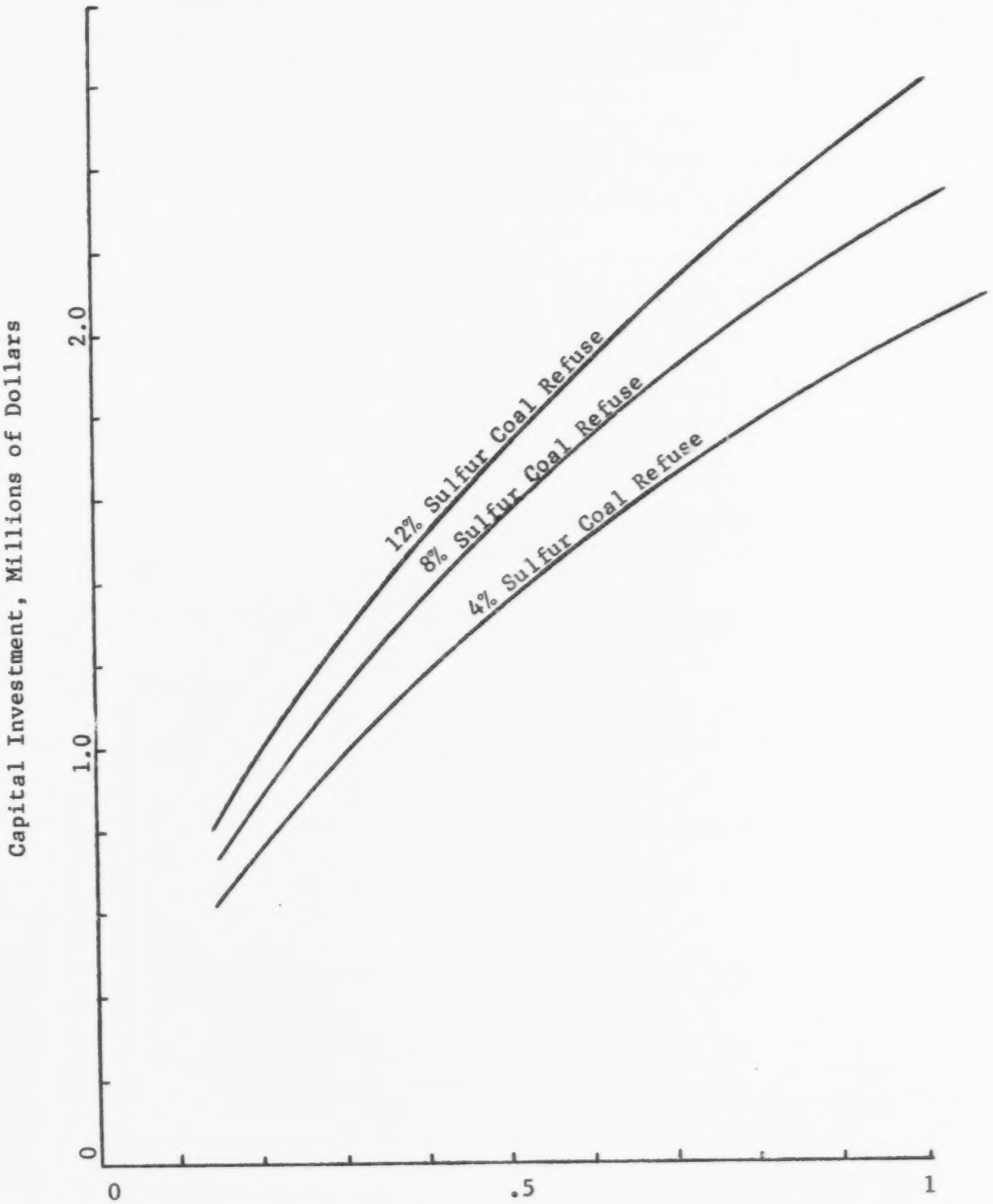

FIGURE 16-CAPITAL INVESTMENT VS. PLANT CAPACITY
FOR VARIOUS COAL REFUSE SULFUR CONTENTS

operating revenue is defined as the revenue resulting from the profits realized from the selling of products less the costs associated with capital interest charges, labor and supervision, maintenance and raw materials. Table 6 was calculated using the material balance shown in Table 4 and the fixed capital requirements of Table 5. This table was prepared assuming that sulfur and ash pellets can be sold for $20/ton and at $1.5/ton respectively and that limestone can be purchased at $2.5/ton.

TABLE 6
OPERATING REVENUE FOR A ONE MM TON/YEAR COAL REFUSE PLANT
(All Numbers, Dollars/Day - 360 Day/Year Basis)

Daily Production Cost	
Capital Interest Charge @ 14%	900
Labor and Supervision (2 men--$50/day - 3 shifts)	300
Maintenance @ 10% of Fixed Capital	642
Coal Refuse (2778 tons @ $0.5/ton)*	1,390
Limestone (695 tons @ $2.5/ton)	1,738
	4,970
Daily Production Credit	
Sulfur (211 tons @ $20/ton)	4,220
Ash Pellets (1824 tons @ $1.5/ton)	2,736
	6,956
Operating Revenue	1,986
Return on Investment (yearly profit before taxes/capital investment)	31%
Payback Period (capital investment/yearly profit before taxes)	3.2 years

*Note: This is a charge for coal refuse which coal producers would not have.

At present, the cost of coal refuse is unknown; therefore, a conservative haulage charge of $0.5/ton was assumed for a non-coal producer using the process. This haulage charge assumes the coal producer will bear the cost of loading the coal refuse on trucks which he would do anyway if he were to stockpile his refuse. As seen in Table 6, the operating revenue is $1986/day which yields a before-tax return on investment of 31 percent. The economic attractiveness of the process should encourage the utilization of coal refuse rather than stockpiling which generates air and water pollution problems.

The operating revenue and the before-tax return on investment (ROI) are a function of plant capacity, coal refuse sulfur content, selling price of sulfur and ash pellets, coal refuse cost, and capital interest rate. In Figures 17-19 are shown the relative effects of these variables on ROI. The effect of the selling price of sulfur and ash pellets is shown in Figure 17 for a one MM ton/year-eight percent sulfur coal refuse plant. As seen, these economic variables have a significant effect upon ROI. For example, the ROI is 15, 31, and 47 percent for sulfur selling prices of 15, 20, and $25/ton respectively for ash pellets sold at $1.5/ton. At present, the selling price of sulfur is in the $20-25/ton range; therefore, ROI's in the range of 31-47 percent are anticipated. The selling price of ash pellets is an important economic consideration. In the economic analysis of the process, a conservative estimate of $1.50/ton for ash pellets as a road aggregate was used. However, these ash pellets will contain lime, ash, and iron and can be more profitably used for other industrial applications. Based on the lime content of the ash pellet alone (approximately 20 percent lime) they can be valued at approximately $3.5/ton. The selling price of ash pellets will depend on the location of the plant and whether suitable users of ash pellets are in close proximity to the plant. Using a conservative maximum selling price of $3/ton, Figure 17 indicates that the ROI increases from 31 to 73 percent as the ash pellet selling price increases from 1.5 to $3/ton.

The effect of the purchase cost of coal refuse on ROI is shown in Figure 18 for a one MM ton/year-eight percent sulfur coal refuse plant at various capital interest charges. It is anticipated that coal refuse will be available to the process at 0 to $0.5/ton depending on who is operating the process (for coal producers the cost would be zero) and the distance the coal refuse must be hauled. As seen in Figure 18, the ROI at a capital interest rate of 14 percent is 53 and 31 percent as the coal refuse cost increases from 0 to $0.5/ton. In the economic evaluation presented in Table 6, a conservative coal refuse cost of $0.5/ton was used.

As expected, the ROI decreases as the capital interest rate increases. This is shown in Figure 18 where the ROI decreases from 39 to 24 percent as the capital interest rate increases from 6 to 20 percent at a coal refuse cost of $0.5/ton. The capital interest rate will depend on who is financing the plant. Municipalities will probably be able to finance at the six percent rate using bonds whereas non-government financing will be at the 14 percent rate.

Figure 19 shows the effect of plant capacity and coal refuse sulfur content on ROI. As seen, as the sulfur content increases from 4 to 12 percent, the ROI increases from 8 to 47 percent for a one MM ton/year plant. Also the ROI increases from 4 to 47 percent as the plant capacity is increased from 0.2 to one MM ton/year for a 12 percent sulfur coal refuse. These results indicate that as large a plant as practical should be built using coal refuse with a maximum of sulfur.

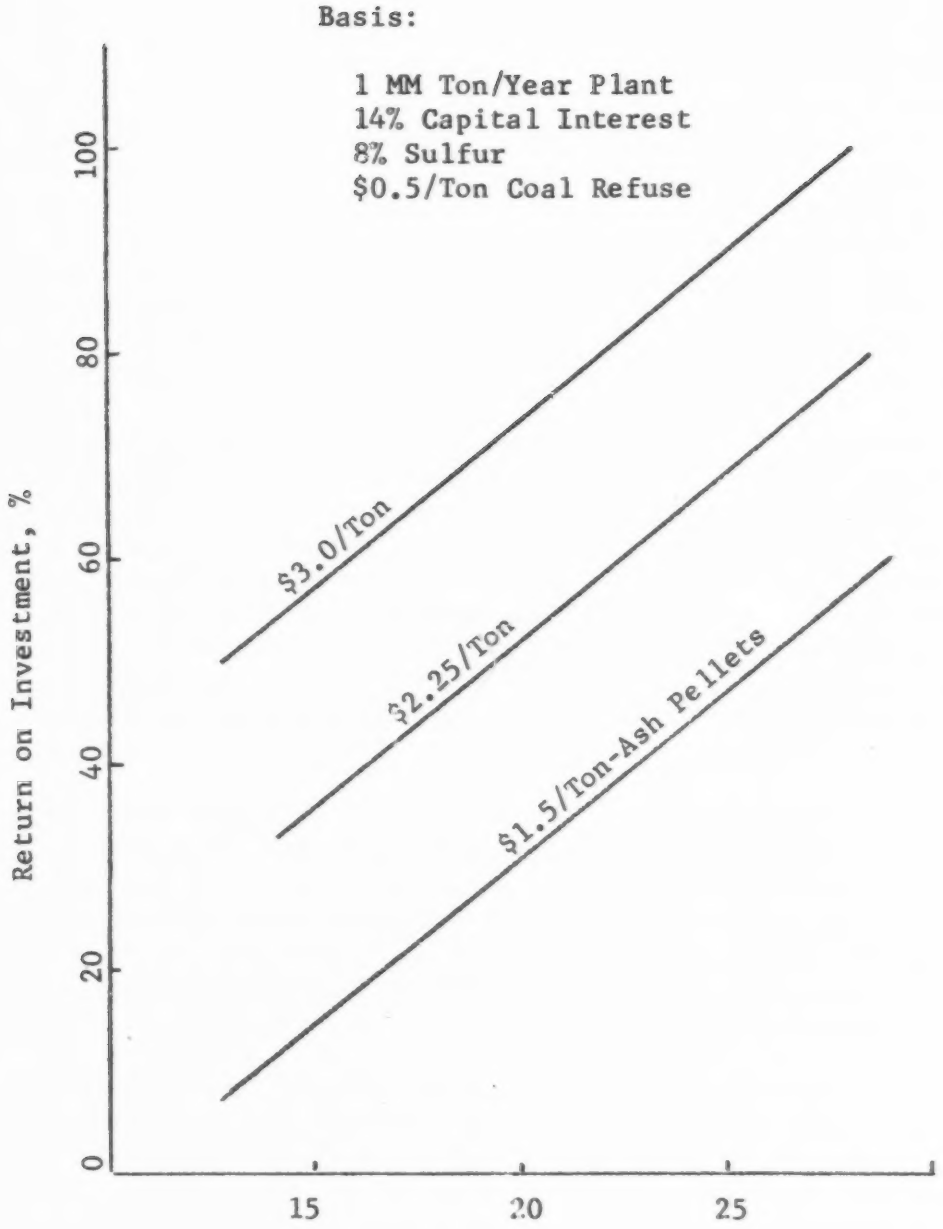

FIGURE 17 -RETURN ON INVESTMENT VS. SULFUR SELLING PRICE AT VARIOUS ASH PELLET SELLING PRICES

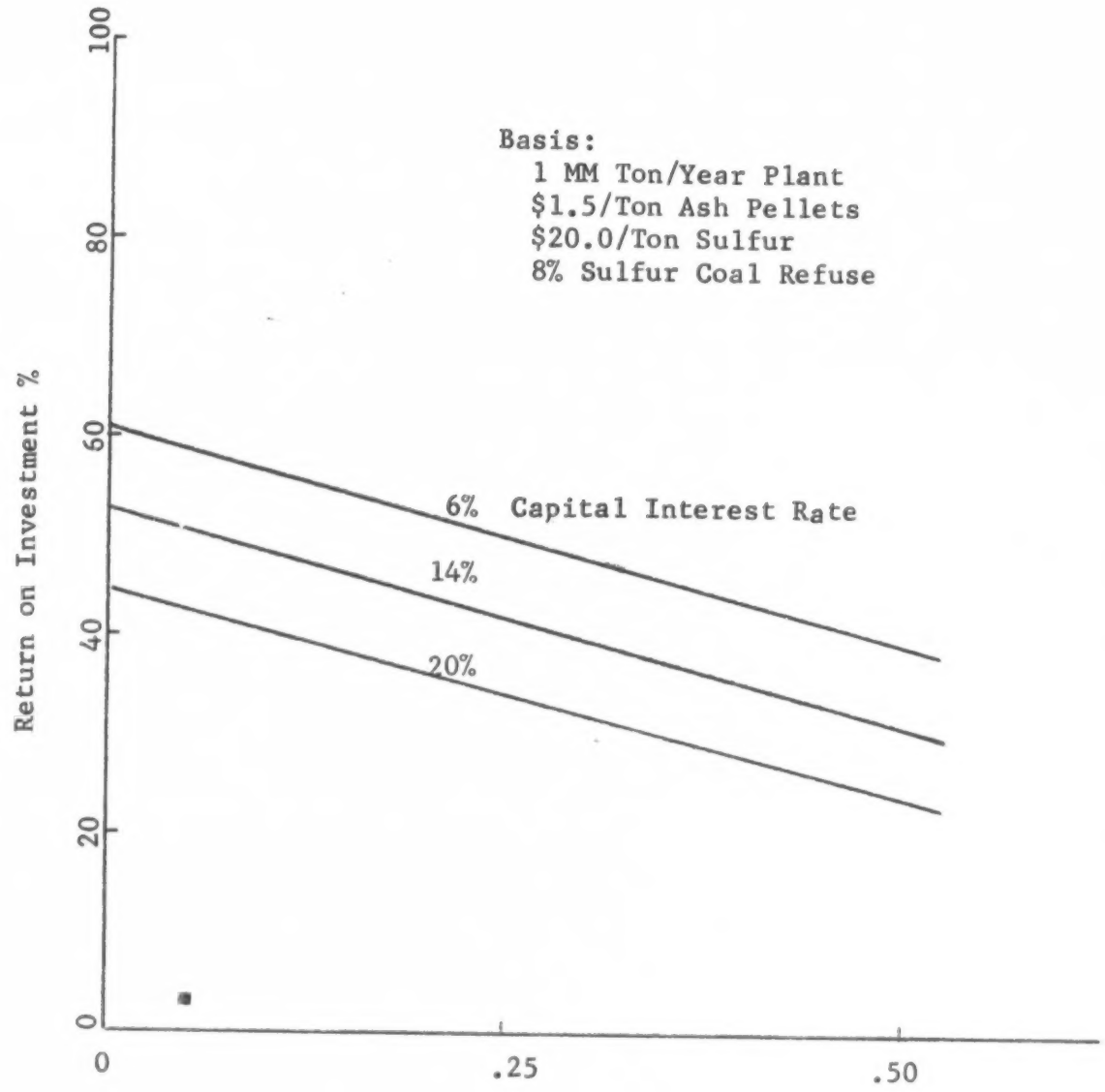

FIGURE 18-RETURN ON INVESTMENT VS. COST OF COAL REFUSE AT VARIOUS CAPITAL INTEREST RATES

Basis:

14% Capital Interest
$1.5/Ton Ash Pellets
$20/Ton Sulfur
$0.5/Ton Coal Refuse

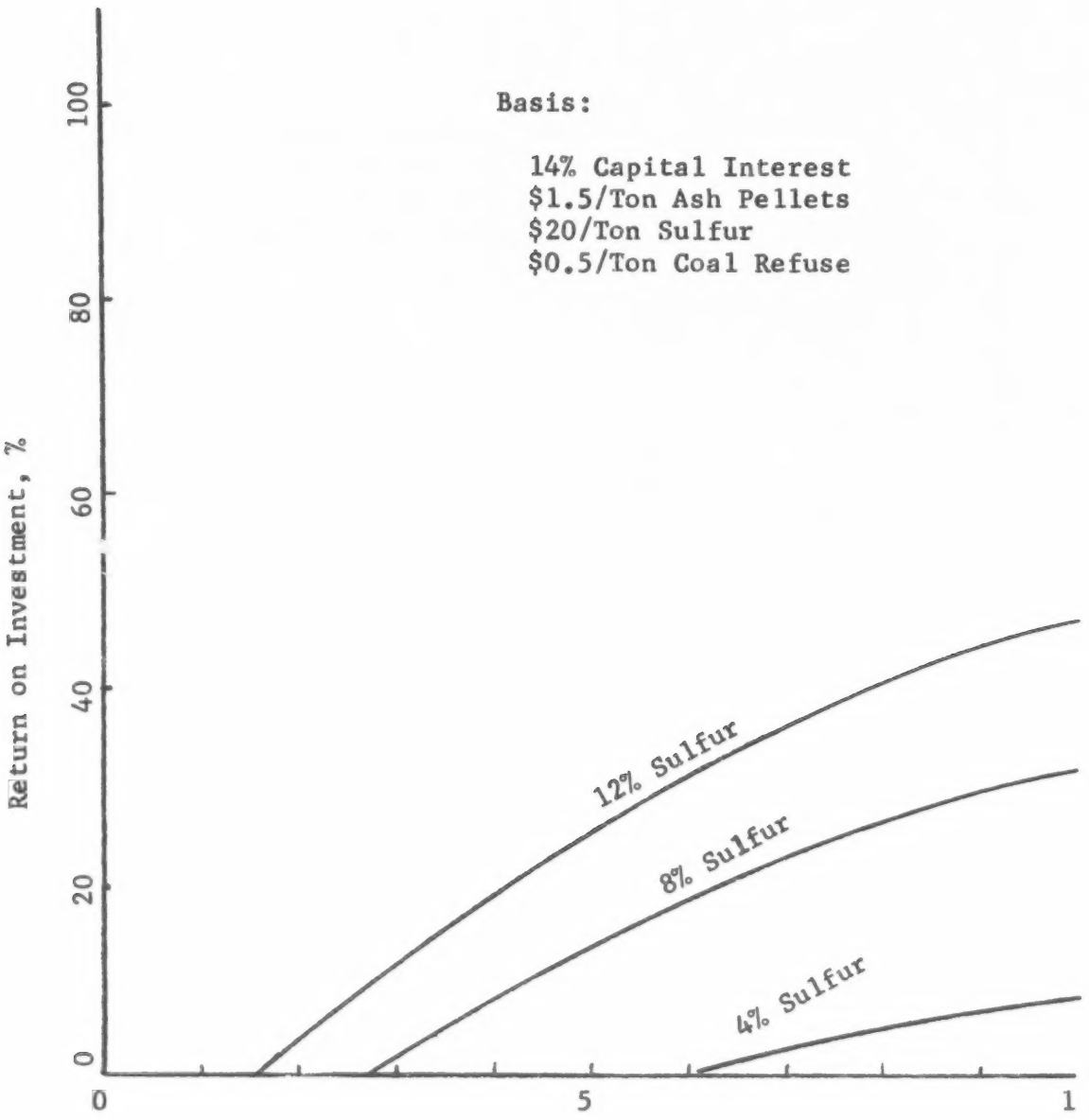

FIGURE 19-RETURN ON INVESTMENT VS. PLANT CAPACITY
AT VARIOUS COAL REFUSE SULFUR CONTENTS

Comments

If a coal producer should utilize the process on his site, the cost of coal refuse would be zero. In fact, the cost of coal refuse could even be considered a credit since the coal producer would not have to stockpile his current production of coal refuse. Assuming the cost of coal refuse to be zero (for a coal producer), the process becomes extremely attractive. Using the data of Table 6, the operating revenue becomes $3376/day ($1986 + $1390 savings in coal refuse cost per day) with a before-tax return on investment of about 53 percent. The coal producer has, therefore, been given great incentive to utilize his coal refuse production. A municipal agency wishing to build a coal refuse plant could obtain capital at a conservative rate of 6 rather than 14 percent. Based on capital available at six percent, and using the data of Table 6, the operating revenue becomes $2490 per day ($1986 + $504 savings in capital interest charges per day). This represents a return on investment of about 39 percent. The economics of the process are extremely favorable and should induce communities or coal producers, saddled with coal refuse piles, to utilize this process and eliminate a serious pollution problem.

Thus far, the discussion has concentrated on the profits that can be realized on this pollution abatement process; however, many communities or small coal producers have coal refuse piles or sources which are of moderate quantity and sulfur content. To eliminate or minimize acid water formation from coal refuse piles under these conditions, the concept of a break-even process operation will be considered. Under a given set of economic and process operating factors, there will exist a plant capacity and coal refuse sulfur content in which the ROI is zero: a break-even operation. In Figure 20 the break-even plant capacity is shown as a function of the coal refuse sulfur content under various economic conditions. For this figure, the selling prices of sulfur and coal refuse have been fixed at $20 and $1.5/ton respectively. Four cases have been considered in which the costs of coal refuse and capital interest rate have been related to the following situations:

Case	Cost of Coal Refuse $/ton	Capital Interest Rate, Percent
I	$0.5	14
II	0.5	6
III	0.	14
IV	0.	6

Case I is for private financing at normal interest rates. From Figure 20 it is seen that the minimum or break-even plant capacity ranges from 640,000 to 160,000 tons/year of coal refuse of 4 to 12 percent sulfur respectively. Case II is for public financing of a plant at a low interest rate (municipal bonds). As seen, break-even plant capacities range from 400,000 to 80,000 tons/year (coal refuse sulfur

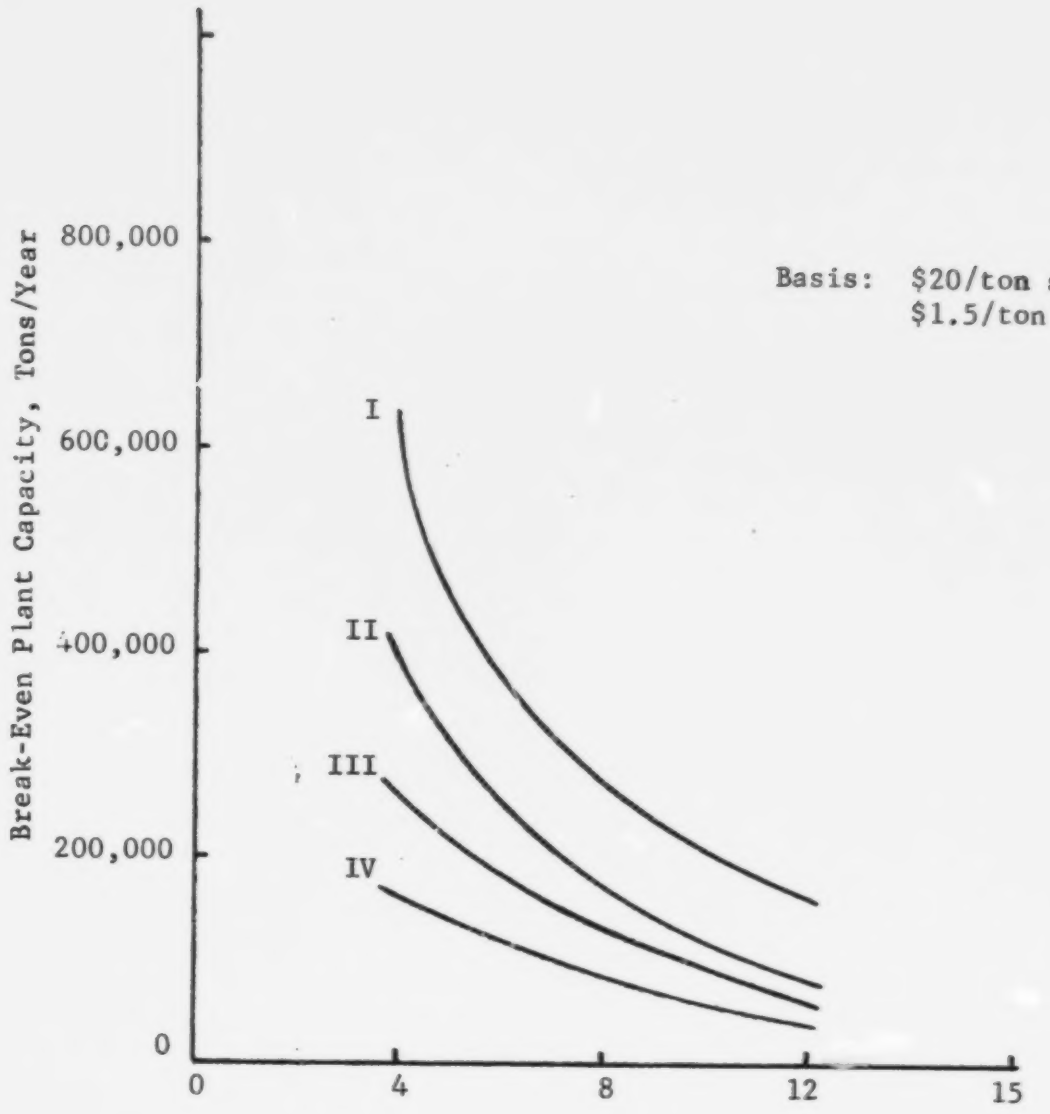

FIGURE 20-BREAK-EVEN PLANT CAPACITY VS. COAL REFUSE SULFUR CONTENT FOR VARIOUS ECONOMIC SITUATIONS

content of 4 to 12 percent). Case III is for private financing at a normal interest rate and no charge for the coal refuse. In this case, the break-even plant capacity varies from 260,000 to 60,000 tons/year. Case IV is for a municipality financing the plant at a low interest rate with no charge for the coal refuse. This is the most attractive situation and yields a break-even plant size of 160,000 to 40,000 tons/year for sulfur contents of 4 to 12 percent. The above results (particularly case IV) indicate that the process can be applied as a no-cost pollution abatement process for communities or small coal producers troubled with moderate to small quantities of low sulfur coal refuse.

SECTION X

ACKNOWLEDGEMENTS

The support of the project of the Environmental Protection Agency and the help provided by Mr. Robert B. Scott, Project Officer, is acknowledged with sincere thanks.

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SECTION XI

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SECTION XII

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APPENDIX A

DETERMINATION OF SULFIDE CONTENT OF COAL REFUSE PELLETS

The determination of sulfur in the coal refuse pellets which is present as either FeS or CaS is based upon the fact that these species react in an acidic media to form hydrogen sulfide. The reactions are as follows:

$$FeS + 2HCl \longrightarrow FeCl_2 + H_2S$$
$$CaS + 2HCl \longrightarrow CaCl_2 + H_2S$$

By determining the H_2S evolved, the total amount of sulfides present in the sample can be determined. Unreacted pyritic sulfur, FeS_2, which may be present in the coal refuse is insoluble in HCl and does not interfere in the method. The amount of hydrogen sulfide evolved is determined by passing the gas through an aqueous $CuSO_4$ solution. Hydrogen sulfide reacts with $CuSO_4$ to form H_2SO_4 and an insoluble precipitate of CuS according to the following equation:

$$H_2S + CuSO_4 \longrightarrow H_2SO_4 + CuS$$

The solution is then filtered to remove the insoluble CuS and titrated with ethylenediaminetetraacetic acid (EDTA) to determine the amount of copper ion that remains in solution. The difference between the amount of copper ion that remains in solution and the amount originally present determines the amount of CuS precipitated and, therefore, the amount of H_2S evolved from the sample. The EDTA titration is a complexiometric titration and is widely used to determine various ions in solution. A complete explanation of the theory and practice of EDTA titrations is given by Flaschka[3] and Fritz[4].

The experimental setup used to determine the amount of sulfides contained in the coal refuse pellets is shown in Figure 1. The sample pellet is ground to approximately minus 100 mesh and placed in an evolution flask. A dropping funnel containing concentrated hydrochloric acid is inserted into a neck of the flask. Nitrogen is used to slowly force the HCl solution into the evolution flask. After the acid has been added to the flask, the heating mantle is turned on and the solution gently refluxed for 30 minutes. Nitrogen continually flows through the system during this analysis to purge the lines of any residual hydrogen sulfide. The evolved hydrogen sulfide is passed through a fritted cylinder absorption column containing a measured volume of $CuSO_4$ solution. A small piece of moistened lead acetate paper was placed at the exit of the absorption column. Any H_2S leaving the column would have turned the lead acetate paper from white to a brown-black color. In no instance was this color change experienced. At the end of 30 minutes, the absorption column is removed from the system and the $CuSO_4$ solution containing a black precipitate of CuS filtered. The clear filtrate was then added to a 500 ml volumetric flask and was diluted to volume with distilled water. A 50 ml aliquot was removed with a pipette and placed in a 400 ml beaker. It was found that the end point in the EDTA titra-

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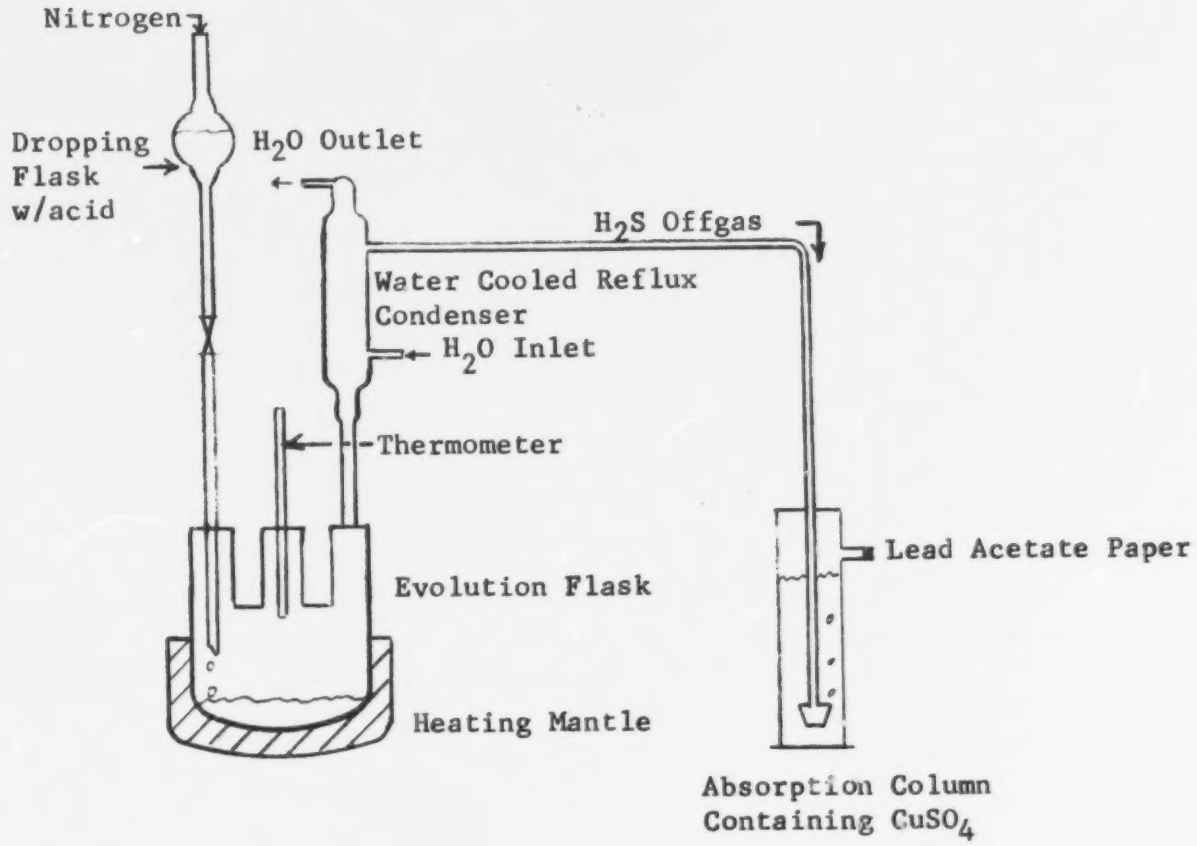

FIGURE 1-SULFIDE DETERMINATION EXPERIMENTAL EQUIPMENT

tion was much sharper if an aliquot was titrated instead of the entire solution. Twenty milliliters of a pH 5.5 buffer solution was added to the aliquot of $CuSO_4$ solution in the beaker. The buffer solution was made by adding 200 g. of ammonia acetate, 80 g. of hexamethylene-tetramine, and 175 ml of glacial acetic acid to 800 ml of distilled water. The buffer solution is used to maintain a constant pH during the EDTA titration. Five drops of PAN indicator (1-(2pyridylazo)-2-Naphthol) and 10-15 drops of xylenol orange indicator were added. The solution is then titrated using a standard solution of EDTA. The end point is reached when the color of the solution turns from a deep blue to green. The EDTA reacts with the copper ion on an equimolar basis. Therefore, the moles of EDTA added are equal to the moles of Cu^{++} remaining in solution. As mentioned previously, the moles of H_2S evolved from the sample are equal to the moles of copper ion consumed in the absorption column. The moles of copper consumed are equal to the number of moles of copper ion initially present less the number of moles present after the evolution of H_2S as determined by the EDTA titration. Once the moles of H_2S are determined, the sulfide content of the sample can be established.

APPENDIX B

DETERMINATION OF DESULFURIZATION OFFGAS COMPOSITION

The second phase of experimentation necessitated the development of an analytical method to determine the amounts of H_2S and SO_2 evolved during desulfurization. The accumulation of these gases in solution was done during experimentation using the apparatus shown in Figure 1 (Section V). A measured amount of $CuSO_4$ solution was placed in an absorption column and the gases exiting the desulfurization experiment were passed through the column. The resulting $CuSO_4$ solution was then analyzed for SO_2 and H_2S using the following procedure.

The experimental procedure consisted of analyzing the $CuSO_4$ solution initially for SO_2 since solutions of SO_2 in water (or in $CuSO_4$ solution) are unstable and release gaseous SO_2 if exposed to the air. Nitrogen is bubbled through the $CuSO_4$ solution to carry the SO_2 into another solution (described below) where it can be directly determined by titration. The analytical apparatus is shown in Figure 1. The $CuSO_4$ solution is gently heated for 45 minutes while the nitrogen purge carries the volatile SO_2 into the indicating solution. The indicating solution is made by adding the following to 100 ml of distilled water: two ml concentrated HCl, one gram of soluble starch (A.C.S. purity), and five grams of potassium iodide (A.C.S. purity). A drop of the potassium iodate titrant will change the solution color from clear to blue due to the formation of a starch-iodine complex. As SO_2 dissolves in the solution, it is oxidized to SO_4 by the iodine, thereby, destroying the starch-iodine complex and blue color. Addition of more titrant restores the blue color. When a persistant blue color is obtained, the end point in the titration has been reached and SO_2 is not issuing from the $CuSO_4$ solution. The stoichiometric reactions involved in the titration are as follows:

$$KIO_3 + 5KI + 6HCl \longrightarrow 3I_2 + 6KCl + 3H_2O$$
$$SO_2 + I_2 + 2H_2O \longrightarrow H_2SO_4 + 2HI$$

The first reaction produces iodine from the potassium iodate titrant. The second reaction depicts the oxidation of SO_2 to H_2SO_4 by iodine and results in the destruction of the blue color (from the starch-iodine complex) until more potassium iodate is added. It can be seen from the above stoichiometry that three moles of KIO_3 titrant added to the solution are equivalent to each mole of SO_2 that dissolves in the solution. Therefore, the amount of SO_2 evolved from the $CuSO_4$ solution is directly related to the number of moles of KIO_3 consumed in the titration.

Approximately 50 percent of the SO_2 that was evolved from the coal refuse pellet was determined by the above method. The remaining SO_2 is dissolved in the $CuSO_4$ solution and will not escape if the solution is filtered or exposed to the air. The next step in the analysis is to filter the insoluble CuS (formed by the reaction of H_2S with $CuSO_4$) from the $CuSO_4$ solution. The clear filtrate is then added to a 500 ml

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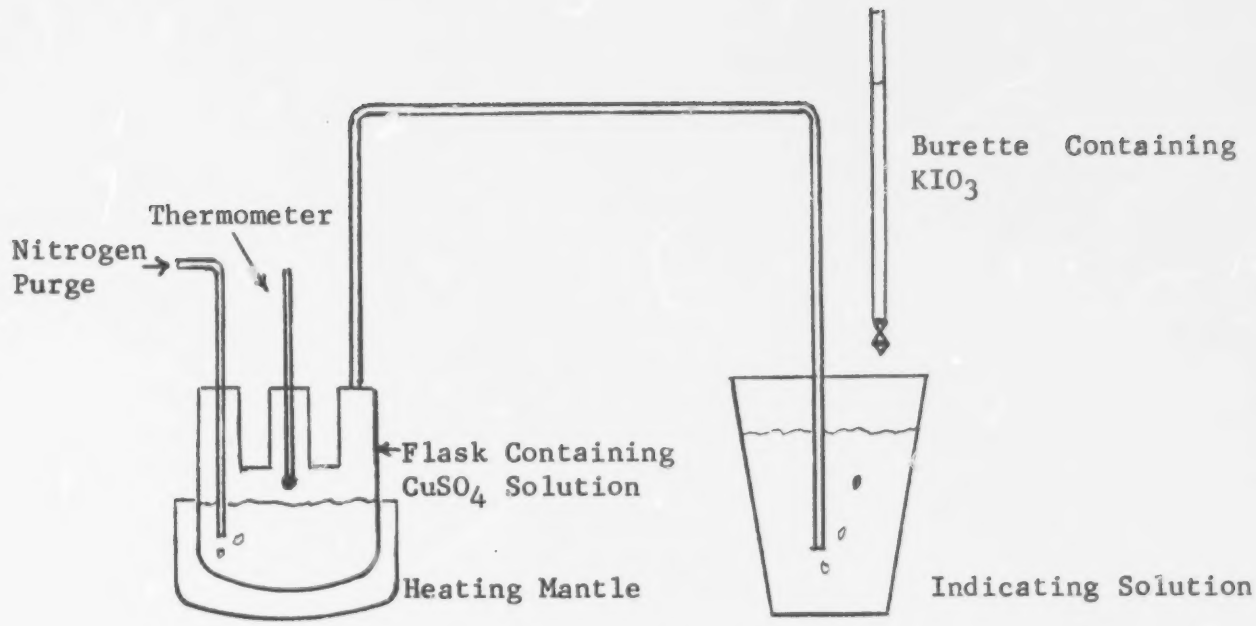

FIGURE 1 -EXPERIMENTAL EQUIPMENT USED IN SO_2 DETERMINATION

volumetric flask and diluted to volume. A 50 ml aliquot is extracted with a pipette and titrated with a standard solution of $KMnO_4$ to determine the amount of dissolved SO_2. The reaction involved in this oxidation titration is as follows:

$$2KMnO_4 + 5SO_2 + 6HCl + 2H_2O \longrightarrow 2MnCl_2 + 2KCl + 5H_2SO_4$$

According to Fischer & Peters[5] the $KMnO_4$ will be completely reduced to $MnCl_2$ if the reaction occurs in a solution with a pH of 1.0 or lower. Therefore, four to five ml of concentrated HCl were added to the 50 ml aliquot to lower the pH to this level. From the stoichiometry of the above reaction, it is seen that five moles of SO_2 react with two moles of $KMnO_4$ titrant. From this ratio and the number of moles of $KMnO_4$ required to complete the titration (an end point is achieved when the solution remains pink for 30 seconds as $KMnO_4$ sets as its own indicator) the amount of dissolved SO_2 can be determined.

The total amount of SO_2 that results from the desulfurization reaction is then the sum of the SO_2 determined by the above procedures. The H_2S is determined in the same manner described in the determination of sulfide sulfur (i.e. an aliquot of the filtered $CuSO_4$ solution is titrated with EDTA).

The amount of elemental sulfur contained in the desulfurization offgas was obtained from a material balance. Sulfur that could not be accounted for as SO_2, H_2S, or residual unreacted sulfides in the pellet was assumed to be in an elemental form.